

NONEQUILIBRIUM FLUCTUATIONS AND TRANSPORT
IN SHEARED FLUIDS

BY

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To my parents.

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TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS.....	iii
ABSTRACT.....	vi
CHAPTERS	
1 INTRODUCTION.....	1
2 PHENOMENOLOGY AND SIMULATION.....	12
Phenomenology.....	12
Experiments.....	13
Simulations.....	15
3 FLUCTUATION MODELS.....	22
Generalized Langevin Equation.....	22
Long Wavelength Fluctuations.....	29
Small Length Scale Fluctuations.....	32
4 LINEARIZED HYDRODYNAMIC MODEL.....	34
Linearized Model.....	34
Green's Function.....	37
Correlation Functions.....	47
Physical Properties.....	52
Probability Densities.....	57
5 NONLINEAR FLUCTUATING HYDRODYNAMICS.....	63
Naive Renormalization.....	63
Formal Renormalization.....	69
Application of Formal Renormalization.....	74
6 SHORT TIME MODEL.....	80
General Properties of the Reduced Distribution Functions.....	80
Explicit Form of Matrix Elements.....	83

	Approximations.....	86
	Hydrodynamic Equations.....	90
7	ANALYSIS OF THE SHORT TIME MODEL.....	96
	Equilibrium Generalized Hydrodynamics.....	96
	Nonequilibrium Generalized Hydrodynamics.....	97
8	CONCLUSIONS.....	121
APPENDICES		
A	LINEARIZATION OF THE LANGEVIN EQUATION.....	125
B	GENERALIZED EIGENVALUE PROBLEM.....	133
C	DYNAMIC STRUCTURE FACTOR.....	139
D	ELIMINATION OF THE THREE POINT FUNCTION.....	142
	BIBLIOGRAPHY.....	146
	BIOGRAPHICAL SKETCH.....	150

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Hydrodynamic fluctuations in a sheared fluid far from equilibrium are described by means of nonlinear stochastic differential equations. Two models resulting from two different limits of the exact Fokker-Planck equation describing hydrodynamic fluctuations in an arbitrary fluid are presented. The first model results from restricting attention to fluctuations which take place on length scales large with respect to the mean free path. The resulting Navier-Stokes-Langevin equations are specialized to shear flow and the associated linear hydrodynamic modes are determined. These are used to calculate the correlation functions of fluctuations around the steady state with the full nonlinear dependence on shear rate necessary for large shear rates. It is then shown how the coupling of the linear modes through the nonlinearities in the stochastic equations allows one to calculate the effect of the nonequilibrium state on the macroscopic transport properties.

The second model results from the short time limit of the exact Fokker-Planck equation and describes fluctuations even on atomic length scales provided the mean free path is small enough. The linear modes of this model are obtained and it is found that they differ considerably from the long wavelength modes. In particular, it is found that at large shear there are two sets of propagating or sound modes. A large shear instability is also found in this model and is tentatively identified with a large shear dynamic phase transition observed in computer simulations of sheared fluids.

CHAPTER 1 INTRODUCTION

Statistical mechanics is a methodology for determining the physical properties of many body systems from the microscopic dynamics of its constituents. It is applicable when the properties one wishes to determine arise as a result of the interaction of a large number of the elementary constituents or when the time scales of interest are large with respect to the typical interaction time of the constituents. When this is the case, attention is shifted from the dynamics of individual constituents to the density in phase space (i.e., the space defined by the degrees of freedom of the system) of the system as a whole which is characterized by the distribution function of the system. The dynamics of the distribution function is given by the Liouville equation, which expresses the conservation of phase space density in a conservative system, together with appropriate boundary conditions, initial conditions and source terms representing the action of nonconservative external interactions.

When the distribution function is constant in time, the system is said to be in a steady state. Equilibrium is the particular steady state obtained by conservative systems and, in general, is unique in that the associated distribution function is known. For this reason, the statistical mechanics of equilibrium systems is well developed and

quite successful at predicting macroscopic properties such as transport equations and thermodynamic susceptibilities.

The statistical mechanics of systems not in equilibrium is, in contrast, poorly understood. This difficulty arises from the fact that nonequilibrium states are difficult to characterize; the distribution function is not known. For systems close to equilibrium linear response theory provides a means of studying nonequilibrium systems by relating their properties to those of equilibrium systems (e.g., fluctuation-dissipation theorems relate transport properties to equilibrium fluctuations). However, far from equilibrium one has only the Liouville equation.

To get a handle on systems far from equilibrium, one typically restricts attention to some subset of the degrees of freedom which obeys an approximately closed dynamics on the length and time scales of interest. Closed, in this context, means that couplings to the degrees of freedom not in the subset being studied are negligible on the average. For example, the macroscopic equations of continuum mechanics for the local conserved densities (e.g., hydrodynamics) often provide an adequate characterization of the nonequilibrium state. The problem then becomes one of determining the average dynamics of these variables (i.e., macroscopic transport equations) and their fluctuations. At present, almost nothing is known about the transport properties of systems far from equilibrium.

This semi-phenomenological approach was first proposed some fifty years ago by Onsager¹ and has essentially been verified for systems near equilibrium.^{2,3} Recently, it has been extended to apply to

systems far from equilibrium,^{4,5} but it is difficult to evaluate the success of such an extension since it has been applied to very few problems. The reason it has not been more thoroughly tested is that its application is straightforward only if the nonequilibrium state is characterized by a few simple macroscopic properties.

One such nonequilibrium system is a simple fluid in a state of uniform shear flow. In uniform shear flow, the pressure and temperature are spatially constant while the flow velocity varies linearly with distance in a direction perpendicular to the flow velocity (Figure 1.1). In a rectangular coordinate system (denoted as x-y-z), the flow field, $\underline{u}_0(\underline{r})$, may be written

$$\underline{u}_0(\underline{r}) = \underline{a} \cdot \underline{r} \quad (1.1)$$

where the shear tensor, $\underline{a}$, is

$$\underline{a} = \hat{a} \hat{x} \hat{y} \quad (1.2)$$

and "a" is the shear rate. The deviation of this system from equilibrium is controlled by a single parameter, the shear rate, giving a simple characterization of the nonequilibrium state.

A sheared fluid is one of the simplest nontrivial nonequilibrium systems imaginable and, indeed, may appear so simple as to be uninteresting. However, even in this simple system drastic effects due to deviations from equilibrium are present, for example in its transport properties, giving the system an intrinsic as well as

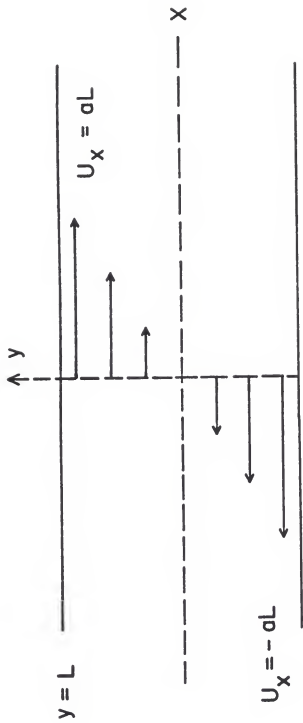


Fig. 1.1 Uniform shear flow.

pedagogical interest. In the remainder of this introduction, we will first describe three anomalies in the behavior of sheared fluids, and then we will describe the methods and physical ideas which will be used to attempt an understanding of the system. The introduction concludes with an outline of the work to be presented.

Sheared fluids are of value as model nonequilibrium systems not only because of the simplicity of the macroscopic state, but also because a great deal of effort has gone into developing methods of simulating such systems on a computer.⁶⁻¹³ This is of prime importance because, as will be discussed in detail later, laboratory experiments involving simple atomic fluids are at present limited to the small shear rate regime (i.e., close to equilibrium). As will be discussed in the next chapter, experiments are possible involving more complex rheological fluids, such as polymeric fluids and glasses,¹⁴ and colloidal suspensions¹⁵ which exhibit many of the properties to be discussed here for simple fluids. We concentrate on simple fluids, however, to simplify the theoretical description. Thus, the only "empirical" data which exist for simple fluids at large shear rates are from simulations. In fact, it is this body of "empirical" results which has spurred most of the recent theoretical interest.^{4,16-25}

The first important anomaly observed in these simulations was associated with the phenomena of shear thinning. As some fluids are sheared, their viscosity drops; they become "thinner" or less viscous. The dependence of viscosity on shear rate had been calculated in 1969 by Yamada and Kawasaki¹⁶ as

$$\eta(a) = \eta_0 - \eta_1 a^{1/2} + O(a). \quad (1.3)$$

The nonanalytic nature of the dependence on the shear rate was previously unsuspected and indicates the breakdown of nonlinear response based on a formal expansion of the Liouville equation in the shear rate. In addition, the result of the simulations was that η_1 was measured to be two orders of magnitude larger than Yamada and Kawasaki¹⁶ predicted. Several other authors¹⁶ calculated η_1 and obtained different numbers, although all are two orders of magnitude too small. A recent proposal by van Beijeren²⁶ for the resolution of this problem will be discussed below.

In 1982, a second anomaly observed in simulations was reported by Erpenbeck.¹² He found that, at very high shear rates, the system passed from the amorphous fluid phase into an ordered phase in which the particles line up one behind another in hexagonally packed "strings" (Figure 1.2). There has recently²⁷ been some debate about the actual nature of the string phase but it is generally agreed that a high shear rate instability, or dynamical phase transition, exists. We shall present below a model exhibiting an instability on atomic scales which matches up qualitatively quite well with that seen in the simulations (note that macroscopic hydrodynamics is believed to be stable for planar shear flow²⁸).

A third anomaly has been reported by Evans⁷ as occurring in two-dimensional fluids. His simulations show the shear viscosity remaining constant as the shear rate increases until at a critical

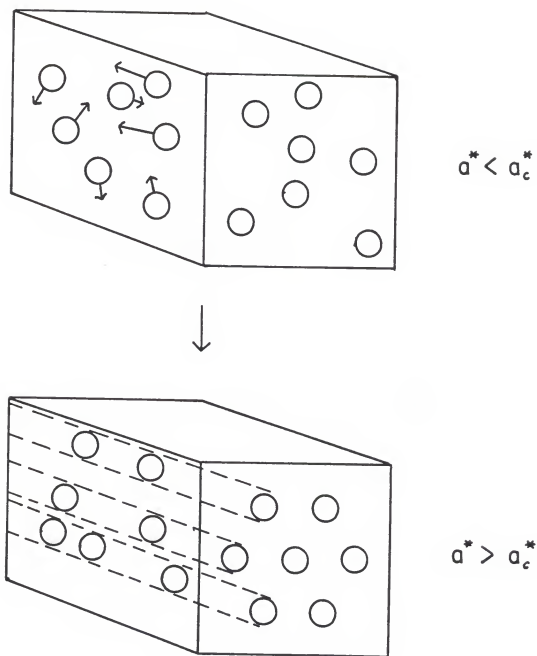


Fig. 1.2 Large shear rate order-disorder transition where a_c^* is the critical shear rate.

shear rate the fluid begins to thin in the expected manner. Evans attributes this to a small shear rate instability for which no theoretical understanding exists as yet. However, the transport properties of two dimensional fluids are anomalous even in equilibrium (two is the critical dimension) leading one to believe that Evans' observations may be related to this fact.

Most of the work to be presented here will consist of an attempt to construct and analyze models of fluctuations around the nonequilibrium state in dense sheared fluids. Once the fluctuations are statistically characterized, one is able to calculate time dependent correlation functions which in turn can be related to observable physical properties of the system. The phenomenological ideas behind this approach are very similar to those in the Einstein-Smolochowski model of Brownian motion.²⁹ One considers the dynamics of the hydrodynamic variables (analogous to the position of the Brownian particle) around the steady state. The hydrodynamic variables are appropriate to describe properties on a scale which is large compared to the microscopic correlation length. Because these variables are the local conserved densities, it is assumed that they decay according to the macroscopic conservation laws (e.g., their time evolution is governed by the Navier-Stokes equations) with the exception that the equations include stochastic sources which represent the thermal noise responsible for the creation of the fluctuations.^{4,30} Finally, the stochastic sources are generally taken to be Gaussian white noise with correlations fixed by a fluctuation-dissipation theorem.

Having these equations, one in principle solves them for the hydrodynamic variables as functionals of the stochastic sources and thus may calculate time dependent correlation functions using the known statistical properties of the sources. As alluded to above, these correlation functions can in turn be used to calculate various physical quantities such as the effect of the steady state on transport coefficients and thermodynamic susceptibilities.

While providing a closed and intuitively appealing model of fluctuations, this description is entirely phenomenological and as such represents an uncontrolled approximation. Several authors^{5,31-33} have addressed the question of the formal derivation and validity of fluctuating hydrodynamics and we shall outline their ideas in a later chapter. The result of these studies is that the foundations and validity of this approach are much better understood.

Thus, one approach to the study of nonequilibrium systems is to replace the microscopic description of the system, as characterized by the distribution function and Liouville's equation, with a hydrodynamic description. A hydrodynamic description of a system is obtained as a result of two approximations. The first is that attention is restricted to the local densities of the conserved variables (e.g., mass, momentum and energy in a simple fluid). On length scales which are large compared to the microscopic correlation length (i.e., the mean free path, ℓ_{mfp}), these variables are expected to decay slowly since their integrals over the whole system do not change at all with time. Thus, on these length scales, these variables are assumed to approximately decouple from the remaining,

quickly fluctuating, microscopic degrees of freedom which give rise to dissipation and thermal fluctuation of the slow variables. Concurrent with this, if k is the wavevector (inverse wavelength or gradient in real space) of the conserved densities, it is required that $(k\ell_{\text{mfp}})$ be small. The equations governing the dynamics of the conserved densities may then be expanded in this small parameter with truncation at second order yielding, for a fluid, the usual Navier-Stokes equations.

In a sufficiently dense fluid, the mean free path is actually smaller than the typical size, σ , of the atoms making up the fluid. In this case, the hydrodynamic description will include terms of all order in $(k\sigma)$ while still expanding in $(k\ell_{\text{mfp}})$. The result is a hydrodynamic description of the (dense) fluid which contains information about the structure of the fluid and is valid on atomic (i.e., $k\sigma \sim 1$) length scales although still restricted to lengths which are large relative to the mean free path ($k\ell_{\text{mfp}} \ll 1$). One might think, and indeed it was long thought, that atomic scale fluctuations require knowledge of all small scale fluctuations; after all, the reason for considering only conserved densities at long wavelengths is that they decay on macroscopic length and time scales while all other fluctuations decay on much shorter, microscopic, scales. However, while studying models of small length scale fluctuations, de Schepper and Cohen³⁴ discovered that even in this regime the conserved densities decayed much slower than other variables and gave the dominant contribution, on these scales, to the density-density correlation function. This indicated that restricting

attention to the hydrodynamic subspace was a valid means of studying fluctuations even on very small length scales. Thus, hydrodynamic models can be used to study even atomic length scale fluctuations provided the mean free path is small enough. In particular, van Beijeren's explanation²⁶ of the discrepancy between theory and simulation results for the size of the shear rate dependent renormalization of the shear viscosity is based on this generalization of fluctuating hydrodynamics to include atomic scale fluctuations in dense fluids.

The work to be presented below consists of modeling hydrodynamic fluctuations as a means of understanding the nonequilibrium state. In Chapter 2, we will discuss experimental and simulational means of studying steady state shear flow and the connection between the two. The third chapter discusses the formal ideas of statistical mechanics used to construct models of nonequilibrium fluctuations and, in particular, to construct fluctuating hydrodynamics at long wavelengths as well as generalized fluctuating hydrodynamics. This is followed by Chapters 4 and 5 analyzing the long wavelength model, the linearized and nonlinear versions respectively, with the aim of deriving various physically observable consequences of the nonequilibrium state. The sixth and seventh chapters contain, respectively, the development and analysis of the small wavelength model and include a discussion of the hydrodynamics and large shear instability occurring on these length scales. The dissertation concludes with a discussion of the results obtained, the completeness of the present description and future directions.

CHAPTER 2 PHENOMENOLOGY AND SIMULATION

In this chapter, we discuss the basic phenomenology, such as length and time scales and strength of shear, which affects the observability of deviations from equilibrium behavior. We then discuss the possibility of performing laboratory experiments which measure nonequilibrium properties. Finally, we discuss the methods of simulating uniform shear flow on a computer.

Phenomenology

In macroscopic hydrodynamics, one typically has three types of parameters: thermodynamic derivatives such as the sound velocity, c_0 , transport coefficients such as the kinematic viscosity, ν_0 , and the wavevector, k , the magnitude of which is inversely proportional to the length scale of the phenomena one is interested in. The time scale of hydrodynamic dissipation is $(\nu_0 k^2)^{-1}$ (in equilibrium, momentum fluctuations dissipate as $e^{-\nu_0 k^2 t}$). In hydrodynamics, one usually uses perturbation theory treating the wavevector as a small parameter. The dimensionless parameter which actually occurs is $(\nu_0 k/c_0)$ thus requiring that $\nu_0 k \ll c_0$ or $\nu_0 k^2 \ll c_0 k$. Physically, this means that the rate of hydrodynamic dissipation is small compared to the rate of sound propagation. This is consistent with the Navier-Stokes's

equations governing hydrodynamics since they are themselves the result of an expansion to second order in the parameter $(k\ell_{\text{mfp}})$, where ℓ_{mfp} is the mean free path, and in fact $c_0/v_0 \sim \ell_{\text{mfp}}$. Typical values of these constants for water at STP³⁵ are $v_0 \sim 1.8 \cdot 10^{-2} \frac{\text{cm}}{\text{s}}$, $c_0 \sim 1.5 \cdot 10^5 \text{ cm/s}$ so $\ell_{\text{mfp}} = 10^{-7} \text{ cm}$. Thus, the applicability of hydrodynamics requires that $k \ll 8.3 \cdot 10^6 \text{ cm}^{-1}$, or $k\sigma \ll 10^{-1}$ where $\sigma \sim 10^{-8} \text{ cm}$ is a typical atomic radius.

When a fluid is sheared, a new time scale, the inverse of the shear rate (denoted here as "a"), is introduced. When the shear rate is as large as the rate of dissipation, we expect that large deviations from equilibrium behavior will occur. For this reason, we refer to a $\sim v_0 k^2$ as the large shear regime. When studying the long wavelength hydrodynamic model, we will require that $a \leq v_0 k^2$ thus including the large shear regime while allowing us to use perturbation theory (since, given this bound, $a \ll c_0 k$).

Experiments

Various methods exist for measuring the static and transport properties of fluids. For example, neutron scattering can be used to measure the static and dynamic structure factors (related to the pair correlation function and transport properties, respectively) on atomic length scales.³⁶ Light scattering samples the dynamic structure factor on hydrodynamic length and time scales.³⁷ These methods and others are available to measure the corresponding properties for nonequilibrium fluids. However, the present ability to test theories of sheared systems is limited by the shear rates which can be obtained

in the laboratory. At present, the largest shear rates reported are less than 10^4 Hz.³⁸ This shear rate is in the large shear regime when $k \sim (a/v_0)^{1/2} \sim 7.45 \cdot 10^2 \text{ cm}^{-1}$. This means that until we look at length scales as large as about 10^{-2} cm the effects of shear will be small compared to the usual equilibrium properties. Thus, light scattering, which measures properties on a length scale of the incident beam's wavelength $\sim 10^{-5}$ cm, and neutron scattering, which is not practical for wavelengths above about 10^{-8} cm, require shear rates about two orders of magnitude larger than those attainable in the laboratory.

There are systems, other than simple fluids, in which similar nonequilibrium effects occur and which have the practical advantage that they have long relaxation times. Because the large shear regime occurs for a $\sim$ inverse relaxation time ($\sim v_0 k^2$ in a simple fluid) it thus becomes accessible in these systems. One example of such a system is a colloidal suspension in which the relaxation time $\tau \sim d^2/D$ for a typical interparticle spacing, d , and diffusion constant of the spheres, D . In this system, the density of spheres determines the relaxation time and the nature of the probe is not restricted as in a simple fluid. Experimental studies of sheared colloidal suspensions have been performed¹⁵ and numerous nonequilibrium phenomena are observed including a string phase similar to that seen in simulations of simple fluids.

Another class of systems exhibiting easily accessible nonequilibrium phenomena is macromolecular (e.g., polymeric) fluids

and glasses.¹⁴ The polymeric systems are not simple fluids because they are composed of anisotropic molecules. However, Simons et al.¹⁴ have shown that strong similarities exist between the phenomena seen in simple and complex fluids. These fluids demonstrate a wide variety of non-Newtonian behaviors including shear thinning. The accessibility of these phenomena again arise due to the fact that the constituents, the macromolecules, have long relaxation times lowering the lower bound of the large shear regime.

In this work, we will restrict our attention to simple fluids. As the preceding discussion indicated, we will not have direct experimental tests of our results. The reason we do not consider colloidal suspensions, polymeric fluids or some other such system is that the results from computer simulations of simple fluids have shown that even our understanding of the simplest system is incomplete. However, because effects, such as shear thinning and the string phase, seen in the simulations are observed in physically related laboratory systems, we have some confidence in the simulations. Thus, we propose to attempt to understand the simplest sheared system and hope, in the process, to gain some understanding by analogy of the more complicated systems in which the nonequilibrium state has important physical consequences.

Simulations

Most of the data for simple fluids have been generated by nonequilibrium molecular dynamics⁶⁻¹³ rather than in the laboratory.

Such simulations require both the establishment of the linear shear profile as well as the maintenance of constant temperature.

In equilibrium molecular dynamics, one considers a box with periodic boundary conditions containing N particles. At each time step in the simulation, one solves the equations of motion (e.g., Newton's equations) for all of the particles and moves them accordingly. The periodic boundary conditions have the effect of decreasing the size (number) dependence of the results allowing one to achieve the bulk, or thermodynamic, limit with on the order of 10^3 particles. In this way, one may study static properties, such as the pair correlation function, and dynamic properties like the decay of correlations. Clearly, simulations have the advantage over experiments in that one can obtain much more data about the system since one has the microscopic state at one's disposal. They are, however, limited by the number of particles, N , and the length of time which can be simulated. In particular, the size restriction limits the smallest wavevectors which can be studied.

The linear shear profile is generated by modifying the simple periodic boundary conditions of equilibrium simulations. The system remains periodic in the x and z directions but when a particle with momentum $\underline{p}$ passes through the $y = L$ plane at time t and with coordinates (x, L, z) , it is reentered at $y = 0$ with coordinates $(x - aLt, y, z)$ and momentum $\underline{p} - ma\hat{x}$. These boundary conditions are known as Lees-Edwards' boundary conditions. They become more transparent when expressed in the local rest frame coordinates, $\tilde{q}$ and $\tilde{p}$, defined as

$$\tilde{\underline{q}} = \underline{q} - \underline{a} \cdot \underline{q}t$$

$$\tilde{\underline{p}} = \underline{p} - m\underline{a} \cdot \underline{q}. \quad (2.1)$$

In these coordinates, the local flow velocity is zero and it is seen that the Lee-Edwards' conditions correspond to simple periodic boundary conditions in the rest frame.

The temperature, T , is a measure of energy fluctuations around the steady state and is defined by

$$\begin{aligned} \frac{3}{2} Nk_B T &= \left\langle \frac{1}{2m} \sum_{i=1}^N (\underline{p}_i - m\underline{a} \cdot \underline{q}_i)^2 \right\rangle \\ &= \left\langle \frac{1}{2m} \sum_{i=1}^N (\tilde{\underline{p}}_i)^2 \right\rangle, \end{aligned} \quad (2.2)$$

where k_B is Boltzmann's constant. Substitution of the conditions of spatially uniform shear flow into the Navier-Stokes equations shows that a sheared fluid will undergo viscous heating. Specifically, one finds that

$$\frac{\partial \epsilon}{\partial t} = \eta a^2, \quad (2.3)$$

where ϵ is the internal energy density, leading to

$$\epsilon(t) = \epsilon(0) + \eta a^2 t. \quad (2.4)$$

For water sheared at 10^4 Hz at STP this leads to a heating rate of 0.024 K/s. For temporally uniform shear flow, particularly for the very high shears applied in computer simulations, an external, nonconservative force is necessary to hold the temperature constant. This heat extracting interaction is called a thermostat. This is equivalent to adding a drag force to the equations of motion:

$$\frac{d}{dt} \underline{q}_i = \underline{p}_i / m$$

$$\frac{d}{dt} \underline{p}_i = \underline{F}_i - \lambda(\Gamma) \tilde{\underline{p}}_i$$

$$\lambda(\Gamma) = \sum_j \tilde{\underline{p}}_j \cdot (\underline{F}_j - \underline{a} \cdot \underline{p}_j) / \sum_j \tilde{\underline{p}}_j^2. \quad (2.5)$$

where the form of $\lambda(\Gamma)$ has been chosen to hold the temperature as defined in eq. (2.2) constant.

The equation of motion form for the thermostat is important because, with the Lee-Edwards' boundary conditions for imposing the flow field, the simulations can be mapped onto a well defined mathematical problem: the solution of Liouville's equation, modified to account for the thermostat, with the imposed boundary conditions. The modified Liouville equation is obtained from the general form of Liouville's theorem,³⁹

$$\left[\frac{\partial}{\partial t} + \frac{1}{m} \underline{p}_i \cdot \frac{\partial}{\partial \underline{q}_i} + \underline{F}_i \cdot \frac{\partial}{\partial \underline{p}_i} \right] \rho(\Gamma, t) - \frac{\partial}{\partial \underline{p}_i} \cdot [\lambda(\Gamma) \tilde{\underline{p}}_i \rho(\Gamma; t)] = 0 \quad (2.6)$$

where the repeated index, i , is to be summed and runs from 1 through N and the dot indicates an ordinary vector scalar product. So, (2.6) may be rewritten as

$$\frac{\partial}{\partial t} \rho + \hat{\tilde{E}} \rho = 0, \quad (2.7)$$

with

$$\hat{\tilde{E}} = \hat{\tilde{E}}_0 + \hat{\tilde{E}}_{\text{int}} + \hat{\tilde{E}}_{\text{ext}} \quad (2.8)$$

where the free streaming and interaction terms are, respectively,

$$\begin{aligned} \hat{\tilde{E}}_0 &= \mathbf{p}_1 \cdot \frac{\partial}{\partial \mathbf{q}_1} \\ \hat{\tilde{E}}_{\text{int}} &= \mathbf{F}_1 \cdot \frac{\partial}{\partial \mathbf{p}_1} \end{aligned} \quad (2.9)$$

while the external term, due to the nonconservative thermostat, acts on the distribution function as

$$\hat{\tilde{E}}_{\text{ext}} \rho(\Gamma; t) = - \frac{\partial}{\partial \mathbf{p}_1} \cdot [\lambda(\Gamma) \tilde{\mathbf{p}}_1 \rho(\Gamma, t)]. \quad (2.10)$$

Because this operator includes the nonconservation of volume in phase space due to the nonconservative force (Liouville's theorem states that $\frac{d}{dt} (\rho(\Gamma) d\Gamma) = 0$ and with nonconservative forces $\frac{d}{dt} d\Gamma \neq 0$), it has a different form when acting on any other phase function.

Specifically, if $A(r)$ is an arbitrary phase function, we have that

$$\hat{\mathcal{E}}_{\text{ext}} A(r) = -\lambda(r) \bar{p}_1 \cdot \frac{\partial}{\partial p_1} A(r). \quad (2.11)$$

The bar indicates the difference between these operators and we note that $\hat{\mathcal{E}}_0 = \hat{\mathcal{E}}_0$. It is easy to see that $\hat{\mathcal{E}}$ and $\hat{\bar{\mathcal{E}}}$ are adjoints with respect to phase space integration.

Finally, we should mention that when working with hard spheres, the potential is singular and the interparticle force, F_i , appearing in these equations ill defined. This difficulty is eliminated by replacing the interaction term with the so-called T-operators which generate the singular hard sphere dynamics. Henceforth, for hard spheres, we will write

$$\hat{\mathcal{E}}_{\text{int}}^{\pm} = T_{\pm}(p_i, p_j; q_{ij}) \quad (2.12)$$

where $\pm$ refers to forward and backward time equations. The form of these operators can be found in the literature⁴⁰ and, for example,

$$\begin{aligned} T_+(x_1, x_2) A(x_1, x_2) = & -\sigma^2 \int d\sigma \left\{ \theta(-\hat{\sigma} \cdot p_{12}) \frac{\hat{\sigma} \cdot p_{12}}{m} \delta(q_{12} - \underline{r}) \right. \\ & \left. \cdot [\hat{b}_{12} - 1] A(x_1, x_2) \right\} \end{aligned} \quad (2.13)$$

where $x_1 = q_1, p_1$, etc.; σ is the hard sphere diameter, $p_{12} = p_1 - p_2$

and

$$\hat{b}_{12} A(q_1, p_1; q_2, p_2) = A(q_1, p_1 - \hat{\sigma} \hat{\sigma} \cdot p_1; q_2, p_2 + \hat{\sigma} \hat{\sigma} \cdot p_{12}). \quad (2.14)$$

We note here that the T-operators are not self adjoint, as is the interaction term for continuous potentials, eq. (2.9), so their adjoints are denoted with bars as well.

CHAPTER 3 FLUCTUATION MODELS

In this chapter, we discuss the statistical mechanical basis of the models to be analyzed. Specifically, the models we will study will be seen to be two different limits of a general Fokker-Planck equation. The detailed form of the models will also be given.

Generalized Langevin Equation

Our basic approach, as discussed in the introduction, to studying nonequilibrium fluctuations around shear flow is to choose a restricted set of variables whose dynamics we wish to study. At a fundamental level, any classical system of N structureless particles, or atoms, is described by the $6N$ coordinates, collectively called Γ , which are the positions, q_i , and momenta p_i of the atoms (where i ranges from 1 to N). The distribution function of the system, $\rho(\Gamma;t)$, which describes the density of states in phase space, satisfies the Liouville equation,

$$\frac{\partial}{\partial t} \rho(\Gamma;t) + \hat{L} \rho(\Gamma;t) = 0; \quad (3.1)$$

the explicit form of which was discussed in a Chapter 2. The set of restricted variables we choose to study is the set of conserved

densities. These are mass density, $\hat{\rho}(\underline{r})$, energy density, $\hat{e}(\underline{r})$, and momentum density, $\hat{j}_\alpha(\underline{r})$. A caret over a function indicates that it is a phase function. Their definitions are

$$\begin{aligned}\hat{\rho}(\underline{r}) &= \sum_{n=1}^N m \Delta(\underline{r}-\underline{q}_n) \\ \hat{e}(\underline{r}) &= \sum_{n=1}^N \frac{1}{2m} (p_n)^2 \Delta(\underline{r}-\underline{q}_n) + \frac{1}{2} \sum_{n \neq n'}^N V(|\underline{q}_n - \underline{q}_{n'}|) \Delta(\underline{r}-\underline{q}_n) \\ \hat{j}_\alpha(\underline{r}) &= \sum_{n=1}^N p_n \Delta(\underline{r}-\underline{q}_n)\end{aligned}\tag{3.2}$$

where $\Delta(\underline{r})$ is some localized function of $\underline{r}$ (for instance, a Dirac delta function). These variables will be denoted collectively as $\hat{y}(\underline{r})$. Our reasons for choosing this particular set were alluded to in the introduction. At length scales large with respect to the mean free path, we expect that the conserved densities are the only variables with long relaxation times (i.e., long with respect to the collision frequency). Therefore, we expect that the statistical properties of the system at these scales can be adequately described in terms of these variables with the other degrees of freedom being modelled as rapidly varying sources. In dense fluids, the mean free path can be smaller than the atomic dimensions and it is found, as one might guess, that the hydrodynamic variables, or conserved densities, still have long relaxation times and so still, on the average, obey an approximately closed dynamics. Because the other degrees of freedom are more rapidly varying, they may again be modelled as stochastic sources.

In the analysis to follow, it will prove convenient to work with the Fourier transform of the variables in eq. (3.2). This is defined to be

$$\hat{\tilde{y}}(\underline{k}) = V^{-1} \int d\underline{r} e^{i\underline{k} \cdot \underline{r}} \hat{y}(\underline{r}). \quad (3.3)$$

We also note that the vector $\tilde{y}(\underline{k})$ is explicitly,

$$\hat{\tilde{y}}(\underline{k}) = (\hat{\tilde{\rho}}(\underline{k}), \hat{\tilde{e}}(\underline{k}), \hat{\tilde{j}}(\underline{k})). \quad (3.4)$$

For notational convenience, we will write

$$\hat{y}_a \leftrightarrow \hat{\tilde{y}}_a(\underline{k}) \quad (3.5)$$

where the Latin index includes both the vector index α and the wavevector $\underline{k}$. Repeated Latin indices are to be summed. The average of $\hat{y}_a$, or $\hat{\tilde{y}}_a(\underline{k})$, over the nonequilibrium ensemble, $\hat{\rho}(\Gamma; t)$, will be denoted as $\langle \hat{y}_a; t \rangle$ where

$$\langle \hat{y}_a; t \rangle = \int d\Gamma \rho(\Gamma; t) \hat{y}_a \quad (3.6)$$

and are the macroscopic variables one would measure in the laboratory.

In general, one also defines time dependent phase functions, $\hat{y}(\underline{k}; t)$, as

$$\begin{aligned}
\hat{\tilde{y}}_{\alpha}(\underline{k};t) &= e^{-\hat{\tilde{L}}t} \hat{\tilde{y}}_{\alpha}(\underline{k}) \\
&= \hat{y}_{\alpha}(t)
\end{aligned}
\tag{3.7}$$

where

$$\begin{aligned}
\langle \hat{\tilde{y}}_{\alpha}; t \rangle &= \int d\Gamma \hat{y}_{\alpha} e^{-\hat{\tilde{L}}t} \rho(\Gamma; 0) \\
&= \int d\Gamma [e^{-\hat{\tilde{L}}t} \hat{y}_{\alpha}] \rho(\Gamma; 0) \\
&= \int d\Gamma \hat{y}_{\alpha}(t) \rho(\Gamma; 0) \\
&= \langle \hat{y}_{\alpha}(t); 0 \rangle.
\end{aligned}
\tag{3.8}$$

So, the macroscopic variables are the average over an initial ensemble, $\hat{\rho}(\Gamma; 0)$, of $\hat{y}_{\alpha}(t)$. The fluctuations of $\hat{y}_{\alpha}(t)$, denoted as $\delta \hat{y}_{\alpha}(t)$, are defined to be

$$\delta \hat{y}_{\alpha}(t) = \hat{y}_{\alpha}(t) - \langle \hat{y}_{\alpha}(t); 0 \rangle.
\tag{3.9}$$

Because we are restricting attention to the set of variables $\hat{y}(t)$, it is useful to introduce the distribution function of these variables, $p(y;t)$, defined to be

$$p(y;t) = \int d\Gamma' \delta(y-\hat{y}') \rho(\Gamma';t), \quad (3.10)$$

where y is some possible value of the phase function $\hat{y}$. So, for any function of the $\hat{y}$'s, say $A[\hat{y}]$, it is clear that

$$\begin{aligned} \langle A[\hat{y}];t \rangle &= \int d\Gamma A[\hat{y}] \rho(\Gamma;t) \\ &= \int dy A[y] p(y;t). \end{aligned} \quad (3.11)$$

Finally, for a steady state such as uniform shear flow, we have that $\rho_{ss}(\Gamma;t) = \rho_{ss}(\Gamma;0) = \rho_{ss}(\Gamma)$. So,

$$\begin{aligned} \langle \hat{y}_a;t \rangle_{ss} &= \langle \hat{y}_a;0 \rangle_{ss} \\ &= y_{0a}. \end{aligned} \quad (3.12)$$

Grabert et al.⁴¹ show, using the projection operator technique introduced by Zwanzig,⁴² that the distribution $p(y;t)$ satisfies the following exact generalized Fokker-Planck equation,

$$\begin{aligned} \frac{\partial}{\partial t} p(y;t) + \frac{\partial}{\partial y_a} \{ v_a[y] p(y;t) - \int_0^t ds \int dy' D_{ab}[y,y';s] p_{ss}(y') \\ \times \frac{\partial}{\partial y_b'} \frac{p(y';t-s)}{p_{ss}(y')} \} = 0 \end{aligned} \quad (3.13)$$

where $p_{ss}(y)$ is the steady state distribution, $v_a[y]$ is called the drift vector and $D_{ab}[y,y';s]$ is called the diffusion matrix. Repeated Latin indices are again to be summed in (3.13). The functionals v and D are expressed in terms of steady state averages and their detailed form is given in Grabert et al.⁴¹ Here, we only note that

$$\frac{\partial}{\partial y_a} \{v_a[y] p_{ss}(y)\} = 0 \quad (3.14)$$

so $p_{ss}(y)$ explicitly satisfies (3.13).

Associated with (3.13) is an exact generalized Langevin equation for the variables $\hat{y}_a(t)$,

$$\begin{aligned} \frac{\partial}{\partial t} \hat{y}_a(t) - v_a[\hat{y}(t)] + \int_0^t ds \{D_{ab}[\hat{y}(t-s);s] F_b[\hat{y}(t-s)] \\ - \frac{\partial}{\partial \hat{y}_b(t-s)} D_{ab}[\hat{y}(t-s);s]\} \\ = \hat{R}_a(t) \end{aligned} \quad (3.15)$$

where the thermodynamic forces, $F_b[\hat{y}(t-s)]$ are defined in terms of the steady state distribution as

$$F_b[\hat{y}(t-s)] = - \frac{\partial \ln p_{ss}(y)}{\partial y_b} \Big|_{y = \hat{y}(t-s)} \quad (3.16)$$

which also appears in (3.13). The functional v_a is the same as that appearing in (3.13) while

$$D_{ab}[\hat{y};s] = \int dy' D_{ab}[y,y';s]|_{y=\hat{y}}. \quad (3.17)$$

The sources $\hat{R}_a(t)$ have the following constrained averages,

$$\begin{aligned} 0 &= \int d\Gamma' \delta(\hat{y}_a - \hat{y}_a') \hat{R}_a'(t) \hat{\rho}_{ss}(\Gamma') \\ D_{ab}[\hat{y};t] &= \int d\Gamma' \delta(\hat{y}_a - \hat{y}_a') \hat{R}_a'(t) \hat{R}_b'(0) \rho_{ss}(\Gamma') \end{aligned} \quad (3.18)$$

where the hat on $R_a(t)$ indicates it to be a phase function and where a primed function has argument Γ' . The first of equations (3.18) indicates that $\hat{R}_a(t)$ is orthogonal, under the steady state average, to any function of $\hat{y}$ and indicates that the constrained average of $\hat{R}_a(t)$ at fixed $\hat{y}$ is zero. The second of equations (3.18) has the form of a fluctuation-dissipation theorem relating the correlation of the "fluctuating force" to the diffusion matrix.

Now, eq. (3.15) together with properties (3.18) may be modelled as a stochastic differential equation if the sources $\hat{R}_a(t)$ are idealized as stochastic processes, denoted as $R_a(t)$, which have the form,

$$R_a(t) = M_{mn}[\hat{y}] S_n(t) \quad (3.19)$$

where

$$\begin{aligned} \langle S_a(t) S_a(t') \rangle &= \langle \tilde{S}_\alpha(\underline{k}, t) \tilde{S}_\alpha(k', t') \rangle \\ &= (2\pi)^3 \delta(\underline{k} + \underline{k}') \delta(t - t') \Lambda_{\alpha\alpha}, \\ &= \Lambda_{aa} \delta(t - t') \end{aligned} \quad (3.20)$$

where $\Lambda_{\alpha\alpha'}$ is a constant matrix and the amplitudes $M_{mn}[\hat{y}]$ are fixed by the fluctuation-dissipation theorem, eq. (3.18). Finally, the variables $\hat{y}_a(t)$ are replaced by stochastic variables denoted as $y_a(t) = \tilde{y}_a(k, t)$ and the average over the distribution function replaced with that over the stochastic sources,

$$\langle \hat{y}_a(t) \rangle_{ss} \rightarrow \langle y_a(t) \rangle_{R(t)} \quad (3.21)$$

since the variables $y_a(t)$ may be considered to be functionals of the stochastic sources.

Long Wavelength Fluctuations

If we restrict our attention to long wavelength fluctuations, then the preceding Langevin model can be explicitly evaluated. Specifically, we only consider wavevectors such that

$$kl_{mfp} \ll 1. \quad (3.22)$$

In this case, the various functionals appearing in eq. (3.15) may be evaluated in terms of a power series in kl_{mfp} . If we truncate the expansions at second order, then the model may be given explicitly,⁵ in terms of the usual microscopic conservation laws,

$$\frac{\partial}{\partial t} \rho + \nabla \cdot \underline{j} = 0$$

$$\frac{\partial}{\partial t} \underline{e} + \underline{\nabla} \cdot \underline{s} = 0$$

$$\frac{\partial}{\partial t} j_{\alpha} + \frac{\partial}{\partial r_{\beta}} t_{\alpha\beta} = 0 \quad (3.23)$$

where s_{α} and $t_{\alpha\beta}$ are the heat flux vector and stress tensor, respectively. These in turn each have a convective part, a dissipative part and a stochastic part, where the latter represents the stochastic source,

$$\begin{aligned} s_{\alpha} &= e u_{\alpha} + t_{\alpha\beta} u_{\beta} + \lambda_0 \frac{\partial}{\partial r_{\alpha}} T + s_{\alpha}^R \\ t_{\alpha\beta} &= u_{\alpha} j_{\beta} + p \delta_{\alpha\beta} - \eta_0 \Delta_{\alpha\beta\mu} \left(\frac{\partial}{\partial r_{\mu}} u \right) - \kappa_0 \delta_{\alpha\beta} \underline{\nabla} \cdot \underline{u} + t_{\alpha\beta}^R \end{aligned} \quad (3.24)$$

where we have introduced the fluctuating velocity, $u_{\alpha} = \rho^{-1} j_{\alpha}$, the fluctuating pressure and temperature, p and T , and transport coefficients, η_0 , κ_0 and λ_0 . These fluctuating thermodynamic functions and transport coefficients are the same functions of y as one has in equilibrium; i.e.,

$$\begin{aligned} p[y] &= p_e[y] \\ &= p_e[\rho, \epsilon] \end{aligned} \quad (3.25)$$

where p_e is the equilibrium pressure functions and the last line

indicates that p_e depends only on the (local) density and internal energy density, ϵ , where ϵ is given by

$$\epsilon = e - \frac{1}{2} \rho^{-1} j^2. \quad (3.26)$$

The dissipative parts of the heat flux vector and stress tensor are seen to be given by a fluctuating version of Fourier's law and Newton's viscosity law, respectively, where

$$\Delta_{\alpha\beta\mu\nu} = \delta_{\alpha\mu} \delta_{\beta\nu} + \delta_{\alpha\nu} \delta_{\beta\mu} - \frac{2}{3} \delta_{\alpha\beta} \delta_{\mu\nu}. \quad (3.27)$$

Finally, as previously mentioned, the stochastic sources are modelled as Gaussian white noise with covariances determined by the fluctuation-dissipation theorem, eq. (3.18),

$$\begin{aligned} S_{\alpha}^R &= (k_B \lambda_0 T^2)^{1/2} s_{\alpha}(\underline{r}, t) \\ t_{\alpha\beta}^R &= (k_B T \eta_0)^{1/2} s_{1\alpha\beta}(\underline{r}, t) + (k_B T \kappa_0)^{1/2} s_{2\alpha\beta}(\underline{r}, t) \\ \langle s_{\alpha} \rangle &= \langle s_{1\alpha\beta} \rangle = \langle s_{2\alpha\beta} \rangle = 0 \\ \langle s_{\alpha}(\underline{r}_1, t_1) s_{\beta}(\underline{r}_2, t_2) \rangle &= 2 \delta_{\alpha\beta} \delta(\underline{r}_1 - \underline{r}_2) \delta(t_1 - t_2) \\ \langle s_{1\alpha\beta}(\underline{r}_1, t_1) s_{1\mu\nu}(\underline{r}_2, t_2) \rangle &= 2 \Delta_{\alpha\beta\mu\nu} \delta(\underline{r}_1 - \underline{r}_2) \delta(t_1 - t_2) \\ \langle s_{2\alpha\beta}(\underline{r}_1, t_1) s_{2\mu\nu}(\underline{r}_2, t_2) \rangle &= 2 \delta_{\alpha\beta} \delta_{\mu\nu} \delta(\underline{r}_1 - \underline{r}_2) \delta(t_1 - t_2) \end{aligned} \quad (3.28) \quad (3.29)$$

with all other cumulants equal to zero. Equations (3.23) - (3.29) completely specify the fluctuating hydrodynamics model which may be summarized as a Langevin equation for the conserved densities, $\hat{y}_a(t)$, with a deterministic part given by the Navier-Stokes equations, local equilibrium transport coefficients and susceptibilities supplemented by the stochastic sources, eqs. (3.28) and (3.29), which model the excluded degrees of freedom. Finally, we note that this model is given in the language of eq. (3.15) in Appendix A where it should be noted that

$$\frac{\partial}{\partial y_b} D_{ab}[y;t] = 0 \quad (3.30)$$

as is shown by Zubarev and Morozov.⁵

Small Length Scale Fluctuations

In a dense fluid, the mean free path may actually be smaller than the typical atomic length scale, to be denoted here as σ (for a gas of hard spheres, σ would be the hard sphere diameter). In this case, one may study atomic length scale fluctuations with the present methods. However, the evaluation of eq. (3.15) requires care for while we still expand in $(k\ell_{mfp})$ we must keep all orders in $(k\sigma)$. Quantities dependent on $(k\sigma)$ carry information about the small scale structure of the fluid. We can evaluate (3.15) while retaining the desired information regarding the small scale structure by taking its short time limit to obtain

$$\frac{\partial}{\partial t} \hat{y}_a(t) - v_a[\hat{y}(t)] = R_a(t). \quad (3.31)$$

The drift vector is defined to be

$$v_a[\hat{y}(t)] = - \left\{ \langle \delta(y - \hat{y}) \hat{f}_a \rangle_{ss} / \langle \delta(y - \hat{y}) \rangle_{ss} \right\} \Big|_{y=\hat{y}(t)}. \quad (3.32)$$

In general, this is a complicated nonlinear functional of $\hat{y}(t)$.

However, as is explained in Chapter 5, we will only be interested in this functional expanded to second order in the deviations from the stationary state. Thus, we expand as

$$v_a[\hat{y}(t)] = v_a[y_0(\underline{k})] + \delta y_b(t) \cdot \left[\frac{\delta}{\delta y_b(t)} v_a[\hat{y}(t)] \right]_{y_0(\underline{k})} + \text{etc.} \quad (3.33)$$

The first order term is

$$\frac{\delta}{\delta y_b(t)} v_a[\hat{y}(t)] = (\langle \delta y \delta y \rangle_{ss}^{-1})_{bc} \langle \delta y_c \hat{f}_a \rangle_{ss}. \quad (3.34)$$

This model is explicitly evaluated in Chapter 6 and analyzed in Chapter 7. While it may seem strange to study the short time limit of the generalized Langevin equation, it should be noted that similar short time equations have been found to provide qualitatively accurate descriptions of dense fluids even out of the short time regime (an excellent example is the Enskog equation⁴³).

CHAPTER 4

LINEARIZED HYDRODYNAMIC MODEL

In this chapter, we linearize the Navier-Stokes-Langevin equations described in Chapter 3 and use them to calculate various statistical properties of the system. We will do this in such a manner that the results apply for shear rates up to and including the large shear regime as previously defined. Of particular interest will be the hydrodynamic propagators and the two time correlation functions. We will discuss the applications of our results to light scattering experiments and will make contact with the small shear results of other authors. The chapter concludes with a description of various formal statistical properties of the system highlighting the difference of this model from local equilibrium.

Linearized Model

The complete hydrodynamic model was given in Chapter 3, eqs. (3.23) - (3.29), and will not be repeated here. The variables we choose to work with are the mass density, total energy density and momentum. So,

$$y_{\alpha} \leftrightarrow (\rho, e, \underline{j})_{\alpha} \quad (4.1)$$

and we denote the steady state averages of these quantities with subscript naught,

$$y_{0\alpha} \leftrightarrow (\rho_0, e_0, \underline{j}_0)_\alpha \quad (4.2)$$

and the deviations from the steady state, the fluctuations, are denoted by Z_α ,

$$Z_\alpha(\underline{r}, t) = y_\alpha(\underline{r}, t) - y_{0\alpha}(\underline{r}, 0) \quad (4.3)$$

where we also use internal energy density and velocity in place of total energy density and momentum density. Finally, we scale and Fourier transform $Z_\alpha(\underline{r}, t)$, to obtain the variable $\tilde{Z}(\underline{k}, t)$ in terms of which we wish to work,

$$\tilde{Z}_\alpha(\underline{k}, t) = \int d^3r \, e^{i\underline{k} \cdot \underline{r}} Z_\alpha(\underline{r}, t) \quad (4.4)$$

$$\tilde{Z}_\alpha(\underline{k}, t) \leftrightarrow [c_1 \delta \tilde{\rho}(\underline{k}, t), c_2 \delta \tilde{\epsilon}(\underline{k}, t), \hat{e}^{(\alpha)}(\underline{k}) \cdot \tilde{\underline{u}}(\underline{k}, t)] \quad (4.5)$$

$$c_1^2 = \rho_0^{-2} \left(\frac{\partial p_0}{\partial \rho_0} \right) \epsilon_0; \quad c_2^2 = (\rho_0 h_0)^{-1} \left(\frac{\partial p_0}{\partial \epsilon_0} \right) \rho_0 \quad (4.6)$$

where $p_0 = p_{LE}[\rho_0; \epsilon_0]$ is the steady state, macroscopic pressure; $h_0 = \epsilon_0 + p_0$ is the enthalpy density and $\{\hat{e}^{(\alpha)}(\underline{k})\}$ are a set of pairwise orthonormal vectors with $\hat{e}^{(1)}(\underline{k}) = \underline{k}/k = \hat{\underline{k}}$ and ϵ is the internal energy density and $\underline{u} = \rho^{-1} \underline{j}$ is the velocity. The scaling,

(4.6), will simplify the form of the equations below and we emphasize that c_1 and c_2 are equilibrium thermodynamic susceptibilities.

In the course of Fourier transforming and linearizing the equations, we find that we must transform the convective terms which include the operator $\rho_0^{-1} \underline{\underline{1}}_0 \cdot \underline{\nabla}$ which on an arbitrary function $f(\underline{r})$ looks like

$$\rho_0^{-1} \underline{\underline{1}}_0 \cdot \underline{\nabla} f(\underline{r}) = a_{ij} r_j \frac{\partial}{\partial r_i} f(\underline{r}). \quad (4.7)$$

The transform of which is

$$\begin{aligned} \int d^3 \underline{r} \, e^{i \underline{k} \cdot \underline{r}} a_{ij} r_j \frac{\partial}{\partial r_i} f(\underline{r}) &= a_{ij} (-i \frac{\partial}{\partial k_j}) \int d^3 \underline{r} \, e^{i \underline{k} \cdot \underline{r}} \frac{\partial}{\partial r_i} f(\underline{r}) \\ &= -a_{ij} \frac{\partial}{\partial k_j} k_i \tilde{f}(\underline{k}). \end{aligned} \quad (4.8)$$

Thus, it turns out that the form of the linearized equations is

$$\frac{\partial}{\partial t} \tilde{Z}_\alpha(\underline{k}, t) - a_{ij} k_i \frac{\partial}{\partial k_j} \tilde{Z}_\alpha(\underline{k}, t) + H_{\alpha\beta}(\underline{k}; a) \tilde{Z}_\beta(\underline{k}, t) = R_\alpha(\underline{k}, t) \quad (4.9)$$

where R_α represents the stochastic sources which, at linear order, do not depend on the fluctuations, $\tilde{Z}_\alpha$. The details of the linearization including the explicit forms of $H_{\alpha\beta}$ and R_α are given in Appendix A. Equation (4.9) is the primary result of this section. In the following sections, we will analyze the hydrodynamic (i.e., normal) modes described by this equation. For zero shear, $H_{\alpha\beta}$ is the usual

matrix of linearized hydrodynamics the eigenvalues of which describe sound propagation, heat diffusion and momentum diffusion.

An important feature of eq. (4.9) is the coupling of variables of different wavevectors implicit in the gradient term. This unusual feature has important consequences on the evolution of fluctuations and is known as linear mode coupling.

Green's Function

To solve equation (4.9), we introduce the Green's function $G_{\alpha\beta}(\underline{k}, \underline{k}'; t)$ defined to satisfy

$$\frac{\partial}{\partial t} G_{\alpha\beta}(\underline{k}, \underline{k}'; t) - a_{ij} k_i \frac{\partial}{\partial k_j} G_{\alpha\beta}(\underline{k}, \underline{k}'; t) + H_{\alpha\sigma}(\underline{k}; a) G_{\sigma\beta}(\underline{k}, \underline{k}'; t) = 0$$

$$\text{with } G_{\alpha\beta}(\underline{k}, \underline{k}'; 0) = (2\pi)^3 \delta(\underline{k} - \underline{k}') \delta_{\alpha\beta}. \quad (4.10)$$

In equilibrium, i.e., $a = 0$, the solution of (4.10) requires nothing more than the diagonalization of the hydrodynamic matrix $H_{\alpha\beta}$. Before solving (4.10) for nonzero shear, we recall the equilibrium solution.³⁹

Let the eigenvectors of $H_{\alpha\beta}(\underline{k}, a=0)$ be denoted as $\{\underline{\xi}^{(i)}(\underline{k})\}_{i=1,5}$ and the corresponding eigenvalues be $\{\lambda^{(i)}(\underline{k})\}_{i=1,5}$ so that

$$H_{\alpha\sigma}(\underline{k}, 0) \xi_{\sigma}^{(i)}(\underline{k}) = \lambda^{(i)}(\underline{k}) \xi_{\alpha}^{(i)}(\underline{k}). \quad (4.11)$$

Furthermore, as $H_{\alpha\beta}$ is in general nonhermitian, we introduce the biorthogonal set of vectors, $\{\underline{\eta}^{(i)}(\underline{k})\}_{i=1,5}$, defined to satisfy

$$\underline{\eta}^{(i)}(\underline{k}) \cdot \underline{\xi}^{(j)}(\underline{k}) = \delta_{ij}. \quad (4.12)$$

In terms of these functions, the Green's function can be immediately determined to be

$$G_{\alpha\beta}(\underline{k}, \underline{k}'; t) = \sum_{i=1}^5 \xi_{\alpha}^{(i)}(\underline{k}) \eta_{\beta}^{(i)}(\underline{k}') (2\pi)^3 \delta(\underline{k} - \underline{k}') \exp - [\lambda_i(\underline{k})(t - t_0)] \quad (4.13)$$

and t_0 is a constant which can be fixed by an additional boundary condition. The solution to eq. (4.9) is then given by

$$\begin{aligned} \bar{Z}_{\alpha}(\underline{k}, t) = & \int \frac{d\underline{k}'}{(2\pi)^3} G_{\alpha\beta}(\underline{k}, \underline{k}'; t) \bar{Z}_{\beta}(\underline{k}', t_0) \\ & + \int_{t_0}^t d\tau \int \frac{d\underline{k}'}{(2\pi)^3} G_{\alpha\beta}(\underline{k}, \underline{k}'; t - \tau) R_{\beta}(\underline{k}', \tau) \end{aligned} \quad (4.14)$$

where the wavevector integrations extend to infinity.

Because the hydrodynamic matrix $H_{\alpha\beta}$ is the result of a truncation at second order of an expansion in $(k\ell_{mfp})$, the eigenvalues can be determined by perturbation theory in this same small parameter. In equilibrium, one obtains two sound (propagating) modes, a heat mode and two degenerate shear modes,

$$\lambda_1(\underline{k}) = -ic_0k + \frac{1}{2} \Gamma_0 k^2$$

$$\lambda_2(\underline{k}) = ic_0k + \frac{1}{2} \Gamma_0 k^2$$

$$\lambda_3(\underline{k}) = D_{0T} k^2$$

$$\lambda_4(\underline{k}) = \nu_0 k^2$$

$$\lambda_5(\underline{k}) = \nu_0 k^2 \quad (4.15)$$

where explicit forms for the speed of sound, c_0 , the sound damping constant, Γ_0 , and the thermal diffusivity, D_{0T} , will be given later. For the present, we note only that the modes all decay like $\exp(-\text{constant})k^2t$ and that these results can be used to calculate the intensity of scattered light from an equilibrium fluid (as described below). Upon doing so, one obtains the classic Landau-Placzek formula⁴⁴ which is perhaps the most successful application of fluctuating hydrodynamics. In fact, comparison of this result and experiment provides one of the best known means of measuring the equilibrium transport coefficients.

Returning to the nonequilibrium problem, eq. (4.10), we introduce a shear rate dependent generalization of eqs. (4.11) - (4.12) as follows:

$$-a_{ij} k_i \frac{\partial}{\partial k_j} \xi_{\alpha}^{(\ell)}(\underline{k}; a) + H_{\alpha\sigma}(\underline{k}; a) \xi_{\sigma}^{(\ell)}(\underline{k}; a) = \lambda^{(\ell)}(\underline{k}; a) \xi_{\alpha}^{(\ell)}(\underline{k}; a)$$

$$\underline{\eta}^{(i)}(\underline{k}; a) \cdot \underline{\xi}^{(j)}(\underline{k}; a) = \delta_{ij}. \quad (4.16)$$

The presence of the gradient operator in (4.16) greatly complicates the problem. However, as discussed in Chapter 2, we restrict the size of the shear rate by requiring that the rate of convection be no larger than the rate of dissipation yielding the condition,

$$a \leq v_0 k^2. \quad (4.17)$$

This choice is what allowed us to neglect heating in these equations, since the rate of heating goes like $a^2 \sim k^4$ (see eq. 2.3), and makes possible a perturbative solution of eq. (4.16). The details of this calculation are given in Appendix B. The eigenvalues so obtained are

$$\lambda_1 = -ic_0 k + \frac{1}{2} (\Gamma_0 k^2 + ak_x k_y / k^2)$$

$$\lambda_2 = ic_0 k + \frac{1}{2} (\Gamma_0 k^2 + ak_x k_y / k^2)$$

$$\lambda_3 = D_{0T} k^2$$

$$\lambda_4 = v_0 k^2 - ak_x k_y / k^2$$

$$\lambda_5 = v_0 k^2. \quad (4.18)$$

We see that the degeneracy of the shear modes has been lifted while the sound damping constant has been shifted and the heat mode remains unaffected at this order.

If we now write the Green's function as

$$G_{\alpha\beta}(\underline{k}, \underline{k}'; t) = \sum_{i=1}^5 \eta_{\alpha}^{(i)}(\underline{k}; a) \epsilon_{\beta}^{(i)}(\underline{k}'; a) G^{(i)}(\underline{k}, \underline{k}'; t), \quad (4.19)$$

then we find that the function $G^{(1)}$ satisfies the following equation:

$$\left[\frac{\partial}{\partial t} - a_{ij} k_i \frac{\partial}{\partial k_j} + \lambda^{(1)}(\underline{k}, a) \right] G^{(1)}(\underline{k}, \underline{k}'; t) = 0$$

$$G^{(1)}(\underline{k}, \underline{k}'; 0) = (2\pi)^3 \delta(\underline{k} - \underline{k}'). \quad (4.20)$$

This scalar equation is easily solved and if we introduce a time dependent wavevector as

$$k_i(t) = k_i - k_j a_{ji} t = k_i - \delta_{iy} k_x a t, \quad (4.21)$$

then the solution of (4.20) is

$$G^{(1)}(\underline{k}, \underline{k}'; t) = (2\pi)^3 \delta(\underline{k} - \underline{k}'(t)) E^{(1)}(\underline{k}, t)$$

where

$$E^{(1)}(\underline{k}, t) = \exp - \int_{t_0}^t d\tau \lambda_1(\underline{k}(-\tau)). \quad (4.22)$$

The explicit form of the propagators in (4.22) is

$$E^{(1)}(\underline{k}, t) = [k/k(-t)]^{1/2} \exp\{-ic_0 k \alpha(t) - \frac{1}{2} \Gamma_0 k^2 \beta(t)\}$$

$$E^{(2)}(\underline{k}, t) = E^{(1)*}(\underline{k}, t)$$

$$E^{(3)}(\underline{k}, t) = \exp\{-D_{0T} k^2 \beta(t)\}$$

$$E^{(4)}(\underline{k}, t) = [k(-t)/k] \exp\{-v_0 k^2 \beta(-t)\}$$

$$E^{(5)}(\underline{k}, t) = \exp\{-v_0 k^2 \beta(-t)\} \quad (4.23)$$

$$\text{where } \alpha(t) = (2ak_x k)^{-1} \{ (k_y(-t)k(-t) - k_y k)$$

$$+ k^2 \ln \left[\frac{k(-t) + k_y(-t) \operatorname{sgn}(ak_x)}{k + k_y \operatorname{sgn}(ak_x)} \right] \}$$

$$\beta(t) = (ak_x k^2)^{-1} \{ k^2 (k_y(-t) - k_y) + \frac{1}{3} (k_y^3(-t) - k_y^3) \}$$

$$k^2 = k_x^2 + k_z^2. \quad (4.24)$$

These functions behave for long times as

$$\alpha(t) \rightarrow (ak_x/2k)t^2$$

$$\beta(t) \rightarrow \frac{1}{3} (ak_x/k)^2 t^3. \quad (4.25)$$

Because $\lim_{t \rightarrow \infty} \beta(t) > 0$, the modes are all stable as expected (see Drazin and Reid²⁸ and Case²⁸ for further discussion of the stability of macroscopic shear flow).

In order to illustrate the physical significance of some of the shear rate dependent effects described by these equations, consider the evolution of a purely hydrodynamic sound excitation along the direction of flow. Specifically, we take $\tilde{Z}_\alpha(\underline{k}, 0) = \xi_\alpha^{(1)}(\underline{k}) \delta(\underline{k} - \underline{k}_0)$ with $\underline{k}_0 = k_0 \hat{x}$. The evolution of hydrodynamic excitations is given by eq. (4.14) when conditionally averaged over the stochastic force with fixed initial condition $\tilde{Z}_\alpha(\underline{k}, 0)$. Denoting this average by a double bracket we have that

$$\begin{aligned} \langle\langle \tilde{Z}_\alpha(\underline{k}, t) \rangle\rangle &= \int \frac{d\underline{k}'}{(2\pi)^3} G_{\alpha\beta}(\underline{k}, \underline{k}'; t) \tilde{Z}_\beta(\underline{k}', 0) \\ &= \delta(\underline{k} - \underline{k}_0(t)) \xi_\alpha^{(1)}(\underline{k}) E^{(1)}(\underline{k}, t). \end{aligned} \quad (4.26)$$

Inverting the Fourier transforms yields,

$$\begin{aligned} \langle\langle Z_\alpha(\underline{r}, t) \rangle\rangle &= \xi_\alpha^{(1)}(\underline{k}_0(t)) (1 + a^2 t^2)^{1/4} e^{-\Gamma_0 k_0^2 \beta(t, -a)/2} \\ &\quad \times \cos[k_0[x(t) - c_0 \alpha(t, -a)]] \end{aligned} \quad (4.27)$$

where $\alpha(t, a)$ and $\beta(t, a)$ were defined in (4.25) and $x(t) = x + ayt$. The time dependent coordinate $x(t)$ is due to the expected Doppler shift in the sound wave which travels in a moving medium. This kinematic effect may be suppressed by restricting attention to the

$y = 0$ plane and without loss of generality, we may choose $x = 0$ as well. Thus, the remaining shear effects are due to gradients of the velocity field and not the magnitude of the velocity. Figure (4.1) shows $\langle\langle Z_{\alpha}(r=0, t) \rangle\rangle / \langle\langle Z_{\alpha}(0, 0) \rangle\rangle$ for the choice of parameters $(c_0 k_0 / \Gamma_0 k_0^2) = 10^{-1}$, which is typical, and the two cases $(a / \Gamma_0 k_0^2) = 0$ and 1. Note that in the former case,

$$\langle\langle Z_{\alpha}(0, t) \rangle\rangle / \langle\langle Z_{\alpha}(0, 0) \rangle\rangle = e^{-\Gamma_0 k_0^2 t / 2} \cos(c_0 k_0 t) \quad (4.28)$$

which is the expression for ordinary sound propagation. Two effects are easily seen. First, the effective sound velocity increases with time relative to that for zero shear rate on this time scale.

Specifically,

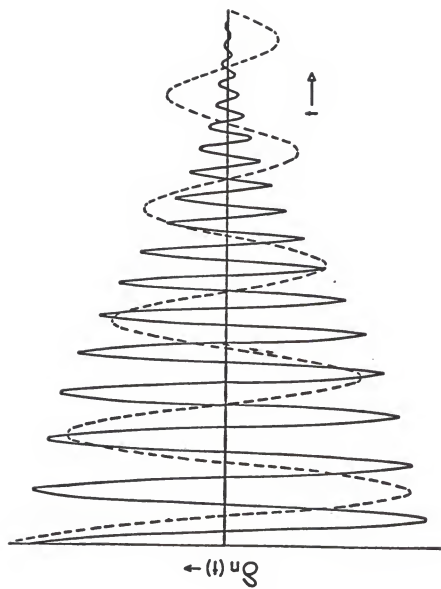
$$\frac{c_0 k_0 \alpha(-t)}{c_0 k_0 t} = \frac{1}{2} \left\{ (1 + \tau^2)^{1/2} + \frac{1}{\tau} \ln[(1 + \tau^2)^{1/2} + \tau] \right\} \quad (4.29)$$

where $\tau = \Gamma_0 k_0^2 t$. Second is that the attenuation is enhanced, relative to that for zero shear, as time increases,

$$\frac{\Gamma_0 k_0^2 \beta(t, -a)}{\Gamma_0 k_0^2 t} = 1 + \frac{1}{3} a^2 \tau^2. \quad (4.30)$$

These relative magnitudes of convection and dissipation would be very difficult to reach with simple fluids but are possible for laboratory colloidal suspensions.

Fig. 4.1 Propagation and damping of sound wave in shear flow for $a/\Gamma_0 k_0^2 = 1$ (—) and for $a/\Gamma_0 k_0^2 = 0$ (---).



Correlation Functions

The correlation functions of the deviations of the fluctuations from the steady state are useful for a number of reasons. From them one may calculate the dynamic structure factor, which describes the intensity of light scattered from the system and transport properties such as the shear rate dependent renormalized viscosities and they characterize the deviation of the system from local equilibrium. In this section, we calculate the two point correlation functions.

The two point correlation functions are defined to be

$$C_{\alpha\beta}(\underline{k}, t; \underline{k}', t'; a) = \langle \bar{Z}_{\alpha}(\underline{k}, t) \bar{Z}_{\beta}(\underline{k}', t') \rangle \quad (4.31)$$

where the brackets denote the nonequilibrium average which in the present case corresponds to an average over the stochastic forces. Time reversal invariance and stationarity require that

$$\begin{aligned} C_{\alpha\beta}(\underline{k}, t; \underline{k}', t'; a) &= C_{\alpha\beta}(\underline{k}, t-t'; \underline{k}, 0; a) \\ C_{\alpha\beta}(\underline{k}, t; \underline{k}', t'; a) &= P_{\alpha} P_{\beta} C_{\beta\alpha}^{*}(\underline{k}', t; \underline{k}, t'-a) \end{aligned} \quad (4.32)$$

where $P_{\alpha} = \pm 1$ is the parity of $\bar{Z}_{\alpha}$ under time reversal. Therefore, we may consider $t \geq 0$ without loss of generality.

If we define

$$F^{(i)}(\underline{k}, t) = \eta_{\alpha}^{(i)}(\underline{k}; a) R_{\alpha}(\underline{k}, t), \quad (4.33)$$

then, using eq. (4.14), we find that

$$\begin{aligned}
 C_{\alpha\beta}(\underline{k}, t; \underline{k}', 0; a) &= C_{\alpha\beta}(\underline{k}, \underline{k}'; t) \\
 &= \sum_{i,j} \int_0^\infty d\tau \int_0^\infty d\tau' \{ \xi_\alpha^{(i)}(\underline{k}) \xi_\beta^{(j)}(\underline{k}') E^{(i)}(\underline{k}, \tau) E^{(j)}(\underline{k}', \tau') \\
 &\quad \times \langle F^{(i)}(\underline{k}, (-\tau), t-\tau) F^{(j)}(\underline{k}'(-\tau'), -\tau') \rangle \quad (4.34)
 \end{aligned}$$

where we have taken $t_0 \rightarrow -\infty$ in eq. (4.14) and used the boundary condition that $\bar{Z}_\alpha(\underline{k}, -\infty)$ is finite. It is clear that

$$\langle F^{(i)}(\underline{k}, t) F^{(j)}(\underline{k}', t') \rangle = (2\pi)^3 \delta(\underline{k} + \underline{k}') \delta(t - t') F^{(ij)}(\underline{k}) \quad (4.35)$$

where the form of $F^{(ij)}(\underline{k})$ is easily determined. Thus,

$$C_{\alpha\beta}(\underline{k}, t; \underline{k}') = (2\pi)^3 \delta(\underline{k} + \underline{k}'(t)) \sum_i \xi_\alpha^{(i)}(\underline{k}) \eta_\beta^{(i)}(-\underline{k}') E^{(i)}(\underline{k}, t) C_{\sigma\beta}(-\underline{k}'; a). \quad (4.36)$$

The functions $C_{\alpha\beta}(\underline{k}; a)$ are related to the equal time condition functions because, in particular,

$$C_{\alpha\beta}(\underline{k}, t=0; \underline{k}'; a) = (2\pi)^3 \delta(\underline{k} + \underline{k}') C_{\alpha\beta}(\underline{k}; a). \quad (4.37)$$

The explicit form of these functions is

$$C_{\alpha\beta}(\underline{k};a) = \int_0^\infty d\tau \sum_{i,j} \{ \xi_\alpha^{(i)}(\underline{k}) \xi_\beta^{(j)}(-\underline{k}) E^{(i)}(\underline{k},\tau) E^{(j)}(-\underline{k},\tau) \\ \times F^{(ij)}(\underline{k}(-\tau)) \}. \quad (4.38)$$

The nonzero elements of $C_{\alpha\beta}(\underline{k};a)$ are given in Tables 4.1 and 4.2.

Some immediate information may be gained from these expressions. In particular, eq. (4.36) shows that the two body correlations decay in the same way, i.e., with the same propagator $E^{(i)}(\underline{k},t)$, as the macroscopic modes. This represents a generalization of Onsager's regression hypothesis to nonequilibrium states. Furthermore, eq. (4.38) is a fluctuation-dissipation theorem for the nonequilibrium system. These statements are more obvious when cast in the form of differential equations:

$$\left[\frac{\partial}{\partial t} - a_{ij} k_i \frac{\partial}{\partial k_j} \right] C_{\alpha\beta}(\underline{k},\underline{k}';t) + H_{\alpha\sigma}(\underline{k};a) C_{\sigma\beta}(\underline{k},\underline{k}',t) = 0 \quad (4.39)$$

$$\left[-\delta_{\alpha\sigma} a_{ij} k_i \frac{\partial}{\partial k_j} + H_{\alpha\sigma}(\underline{k};a) \right] C_{\sigma\beta}(\underline{k};a) + \left[H_{\beta\sigma}(-\underline{k};a) \right] C_{\alpha\sigma}(\underline{k},a) = R_{\alpha\beta}(\underline{k}) \quad (4.40)$$

where $R_{\alpha\beta}(\underline{k})$ is the amplitude of the fluctuating forces,

$$\langle R_\alpha(\underline{k},t) R_\beta(\underline{k}',t') \rangle = \delta(\underline{k}+\underline{k}') \delta(t-t') R_{\alpha\beta}(\underline{k}). \quad (4.41)$$

Equation (4.39) shows more clearly the linear regression law while (4.40) has the usual form of a fluctuation-dissipation relation.

Table 4.1 Equal time correlations.

$$C_{\rho\rho}(\underline{k};a) = k_B T_0 \rho_0^2 x_T [1 + \Delta_1(\underline{k};a)]$$

$$C_{\rho\epsilon}(\underline{k};a) = k_B T_0 h_0 \rho_0 x_T [1 - \frac{\alpha_T}{h_0 x_T} T_0 + \Delta_1(\underline{k};a)]$$

$$C_{\epsilon\epsilon}(\underline{k};a) = k_B T_0 x_T [x_T^{-1} T_0 C_v + [h_0 - T_0 \frac{\alpha_T}{x_T}]^2 + h_0^2 \Delta_1(\underline{k};a)]$$

$$C_{33}(\underline{k};a) = k_B T_0 \rho_0^{-1} [1 + \gamma \Delta_1(\underline{k};a)]$$

$$C_{44}(\underline{k};a) = k_B T_0 \rho_0^{-1} [1 - \Delta_2(\underline{k};a)]$$

$$C_{45}(\underline{k};a) = k_B T_0 \rho_0^{-1} \Delta_3(\underline{k};a)$$

$$C_{55}(\underline{k};a) = k_B T_0 \rho_0^{-1} [1 - \Delta_4(\underline{k};a)]$$

Table 4.2 Nonequilibrium contributions to equal time correlations.

$$\Delta_1(\underline{k}; a) = a\gamma^{-1} \int_0^\infty dt \frac{k_x k_y(-t)}{k^3(-t)} e^{-\Gamma_0 k^2 \beta(-t)}$$

$$\Delta_2(\underline{k}; a) = 2a \int_0^\infty dt \frac{k_x k_y(-t)}{k^2} e^{-2v_0 k^2 \beta(-t)}$$

$$\Delta_3(\underline{k}; a) = a \int_0^\infty dt \left[\frac{2k_x k_y(-t)}{k k(-t)} F(\underline{k}, t) + \frac{k_z}{k} \right] e^{-2v_0 k^2 \beta(-t)}$$

$$\Delta_4(\underline{k}; a) = 2a \int_0^\infty dt F(\underline{k}, t) \left[\frac{k_x k_y(-t)}{k k(-t)} F(\underline{k}, t) + \frac{k_z}{k} \right] e^{-2v_0 k^2 \beta(-t)}$$

$$F(\underline{k}, t) = A(\underline{k}(-t)) - \frac{k(-t)}{k} A(\underline{k})$$

$$A(\underline{k}) = \frac{k_z}{k_x k} \tan^{-1} \left(\frac{k_y}{k} \right)$$

$$\underline{k}(t) = \underline{k} - \underline{k} \cdot \underline{a} t$$

$$k^2 = k_x^2 + k_z^2$$

Physical Properties

We now discuss two physical properties which may be determined from the correlation functions. They are the long range nature of the correlations and the light scattering spectrum.

The density-density equal time correlation function in real space is easily seen to have the form

$$\begin{aligned} C_{\rho\rho}(\underline{r};a) &= \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} C_{\rho\rho}(\mathbf{k};a) \\ &= \ell^{-3} k_B T_0 \rho_0^3 \chi_T [\delta(\underline{r}/\ell) + \ell/r F(\underline{r}/\ell)] \end{aligned} \quad (4.42)$$

where the isothermal compressibility, $\chi_T = \rho^{-1}(\frac{\partial \rho}{\partial p})_T$, and where $\ell = (\Gamma_0/a)^{1/2}$ is a typical length scale associated with the shear rate. The limit $F(\underline{r}/\ell)=0$ yields the usual equilibrium result where the δ -function is an idealization of the atomic scale correlations which actually exist in the fluid. The part proportional to $\underline{r}/\ell$ has been obtained before via an expansion to first order in the shear rate.²⁰ Because of the form of F , this actually requires that $\underline{r}/\ell \ll 1$ and yields

$$F(0) = -a_{ij} r_i r_j / 8\pi \gamma a r^2 \quad (4.43)$$

where $\gamma = c_p/c_v$ is the ratio of specific heats. This does not, as has been claimed,²⁰ however, allow us to conclude that the correlations are long-ranged because it is the product of a short distance expansion. To determine the true nature of the correlations, at large

distances, we consider a somewhat simpler problem than the large- r expansion of $F(\underline{r}, \ell)$. Specifically, we consider

$$\int dy \int dz C_{\rho\rho}(\underline{r}) = \ell^{-1} k_B T_0 \rho_0^3 \chi_T [\delta(x/\ell) + \gamma H(x/\ell)]. \quad (4.44)$$

The part of the correlation function due to the deviation from equilibrium, $H(x/\ell)$, is given by

$$H(x/\ell) = (2\sqrt{\pi})^{-1} \int_0^\infty dt \{ (1 + t^2)^{-3/2} t^{-1/2} (1 + \frac{1}{3} t^2)^{-1/2} \\ \times \exp[-(x/\ell)^2 (4t(1 + \frac{1}{3} t^2))^{-1}] \} \quad (4.45)$$

and for large (x/ℓ) behaves as

$$H(x/\ell) \rightarrow 0.828 (x/\ell)^{-5/3}. \quad (4.46)$$

At short distances, this function is Gaussian and the complete function is shown in Fig. 4.2. It is thus clear that the correlations are in fact long ranged, decaying as a power law.

The second physical property we wish to study with the correlation functions is the intensity of light scattered from the fluid. It can be shown³⁹ that the intensity of light at the point $\underline{r}$ with frequency ω due to the initial scattering of a coherent beam of wavevector $\underline{k}_0$ and frequency ω_0 is given by

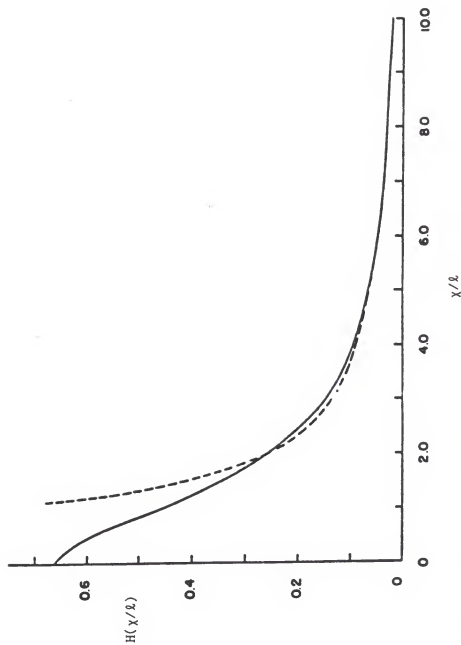


Fig. 4.2 Nonequilibrium contribution, $H(\chi/\lambda)$, to density-density correlation function along direction of flow for $a/r_0 k_0^2 = 1$ (—) and asymptotic form (---).

$$I(\underline{r}, \omega) = \frac{1}{4} I_0 \omega^4 (\alpha/2\pi C_0^2 r) \sin^2 \phi S(\underline{k}, \Omega) \quad (4.47)$$

where I_0 is the spectral intensity of the incoming beam, α is the polarizability of the particles composing the medium,

$\hat{r} \cdot \underline{E}_0 = E_0 \cos \phi$, $\underline{E}_0$ is the amplitude of the coherent beam,

$\underline{k} = \underline{k}_0 - (\omega_0/C_0)\hat{r}$ and $\Omega = \omega - \omega_0$ and where the structure factor,

$S(\underline{k}, \Omega)$, is defined as

$$S(\underline{k}, \Omega) = \int_{-\infty}^{\infty} dt \int \frac{d\underline{k}_1 d\underline{k}_2}{(2\pi)^6} \tilde{\theta}(\underline{k}-\underline{k}_1) \tilde{\theta}(\underline{k}+\underline{k}_2) C_{\rho\rho}(\underline{k}_1 t; \underline{k}_2, 0; a) e^{i\Omega t}. \quad (4.48)$$

Thus, we see that the density-density correlation function determines the intensity of scattered light. The functions, $\tilde{\theta}(\underline{k})$, are Fourier transforms of form factors which limit the volume of integration to that irradiated. In Appendix C, it is shown that $S(\underline{k}, \Omega)$ can be written in terms of nonequilibrium Brillouin and Rayleigh peaks:

$$S(\underline{k}; \Omega) = S_R(\underline{k}; \Omega) + S_B(\underline{k}; \Omega) + S_B(\underline{k}; -\Omega) \quad (4.49)$$

where

$$S_B(\underline{k}; \Omega) = 2\text{Re}\left\{[-i\Omega + \lambda_1(\underline{k}; a) - \frac{1}{2} a_{ij} k_i \frac{\partial}{\partial k_j}]^{-1} C_1^{-2} \xi_1^{(1)} \eta_\alpha^{(1)} C_{\alpha 1}(\underline{k}; a)\right\}$$

$$S_R(\underline{k}; \Omega) = 2\text{Re}\left\{[-i\Omega + \lambda_3(\underline{k}; a) - \frac{1}{2} a_{ij} k_i \frac{\partial}{\partial k_j}]^{-1} C_1^{-2} \xi_1^{(3)} \eta_\alpha^{(3)} C_{\alpha 1}(\underline{k}; a)\right\}.$$

(4.50)

In equilibrium, the gradients are not present and these expressions reduce to simple Lorentzians. Expansion of eqs. (4.19) to first order in the shear rate yields previously obtained results; however, the general evaluation of (4.19) is difficult. A quantity which can be calculated directly is the Landau-Placzek ratio, R , defined as

$$\begin{aligned}
 R(\underline{k};a) &= \int d\omega S_R(\underline{k},\omega) / \int d\omega [S_B(\underline{k},\omega) + S_B(\underline{k},-\omega)] \\
 &= [C_{\rho\rho}(\underline{k};a) - \rho_0/h_0 C_{\epsilon\rho}(\underline{k};a)] / [\alpha^2 C_{\rho\rho}(\underline{k};a) + \rho_0/h_0 C_{\epsilon\rho}(\underline{k};a)]
 \end{aligned}
 \tag{4.51}$$

where $\alpha = \rho_0 c_1 / h_0 c_2$. In particular, the integrated Rayleigh intensity is unchanged from equilibrium,

$$\int d\omega S_R(\underline{k},\omega;a) = (\gamma - 1)/\gamma
 \tag{4.52}$$

where γ = ratio of specific heats. An explicit form of (4.51), obtained using the expressions for the equal time correlation functions given in Appendix C, is

$$R(\underline{k},a) = (\gamma - 1) / [1 + \gamma \Delta_1(\underline{k};a)]
 \tag{4.53}$$

where $\Delta_1 = [C_{\rho\rho}(\underline{k};a) - C_{\rho\rho}(\underline{k};0)]/C_{\rho\rho}(\underline{k},0)$. In Fig. 4.3, we plot $\Delta R = [R(\underline{k};a) - R(\underline{k};0)]/R(\underline{k};0)$ as a function of θ for $\underline{k} = k_0(\cos\theta\hat{x} + \sin\theta\hat{y})$ and $a/\Gamma_0 k_0^2 = 1$. The small shear rate expansion of these results is in agreement with earlier work by Kirkpatrick et al.²⁰ The result, eq. (4.53), is unexpected in that it states that the integrated intensity of the Rayleigh peak is unaffected by the shear.

Probability Densities

In this section, we recast our previous results in the language of the probability distributions of the fluctuations. In particular, the probability distributions are more useful than the description in terms of fluctuations for the calculation of higher order correlation functions or for averages of more general functions.

The probability and joint probability density are defined by

$$P(Z,t) = \langle \delta(\tilde{Z}(t) - Z) \rangle$$

$$P(Z,t;Z',t') = \langle \delta(\tilde{Z}(t) - Z) \delta(\tilde{Z}'(t') - Z') \rangle \quad (4.54)$$

where the averages are taken over the stochastic forces, $\{R_\alpha\}$, and over a specified ensemble of initial values, $\{\tilde{Z}(0)\}$. The δ -functions are short for

$$\delta(\tilde{Z}(t) - Z) \equiv \prod_{\alpha, \underline{k}} \delta(\tilde{Z}_\alpha(\underline{k}, t) - Z_\alpha(\underline{k})). \quad (4.55)$$

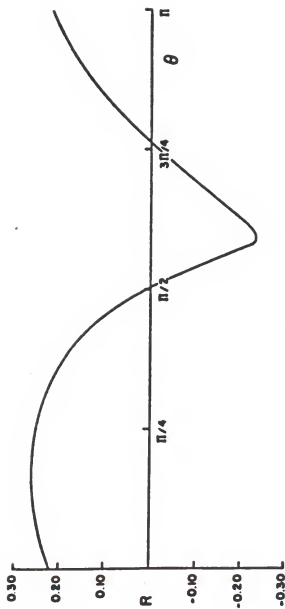


Fig. 4.3 Deviation of the Landan-Placzek ratio, eq. (4.52), as a function of angle for $a/\Gamma k_0^2 = 1$ and $k_z = 0$. The value at $\theta = \pi/2$ corresponds to $k_x = 0$ for which the equilibrium result holds.

We begin the evaluation of eq. (4.54) by calculating a related quantity--the conditional probability density defined by

$$W(Z, t; Z', t') = P(Z, t; Z', t') / P(Z', t'). \quad (4.56)$$

Because the system is being modelled by a Markovian process, the conditional distribution is independent of the initial values, $\{\bar{Z}_\alpha(0)\}$ and because of the neglect of heating, the system is stationary so $W(Z, t; Z', t') = W(Z, t - t'; Z', 0)$. So, without loss of generality, we consider

$$W(Z, t; Z', 0) = \langle \delta(\bar{Z}(t|Z') - Z) \rangle_R \quad (4.57)$$

where, as indicated, the average is only over the stochastic forces and $\bar{Z}(0|Z') = \bar{Z}'$. From eq. (4.14),

$$\bar{Z}_\alpha(t|Z') = G(t)Z' + \int_0^t d\tau G(t-\tau) R(\tau) \quad (4.58)$$

where we have suppressed internal summations. An integral representation of the δ -function in (4.57) and use of (4.58) yields

$$\begin{aligned} W(Z, t; Z', 0) &= \int d\lambda e^{i\lambda \cdot [Z - G(t)Z']} \langle \exp[-i\lambda \cdot \int_0^t d\tau G(t-\tau) R(\tau)] \rangle \\ &= \int d\lambda \exp\{i\lambda [Z - G(t)Z'] - \lambda^2 M\} \end{aligned}$$

$$= \{\det[\pi M(t)]\}^{-1/2} \exp\left\{-\frac{1}{2}[Z-G(t)Z'] \cdot M^{-1}(t) \cdot [Z-G(t)Z']\right\} \quad (4.59)$$

where the second line follows from the first upon use of the Gaussian statistics of the source term. The matrix $M(t)$ is given by

$$M(t) = \int_0^t d\tau \int_0^t d\tau' G(t-\tau) \cdot \langle \underline{R}(\tau) \underline{R}(\tau') \rangle \cdot G^T(t-\tau'). \quad (4.60)$$

Equations (4.39) and (4.40) (the regression law and fluctuation-dissipation theorem) allow us to re-express (4.60) in terms of the correlation function matrix, $C(t) = C_{\alpha\beta}(\underline{k}, t; \underline{k}', 0)$,

$$M(t) = C(0) - C(t) \cdot C^{-1}(0) \cdot C^T(t). \quad (4.61)$$

We can now immediately write down the probability and joint probability densities,

$$P(Z, t) = \int dZ' W(Z, t; Z', 0) P(Z', 0)$$

$$P(Z, t; Z', t') = W(Z, t; Z', t') P(Z', t'), \quad (4.62)$$

where $P(Z', 0)$ is the initial probability density. From (4.61), we can determine the stationary state,

$$P_{ss}(Z) = \lim_{t \rightarrow \infty} P(Z, t)$$

$$= \{\det[\pi C(0)]\}^{-1/2} \exp\left[-\frac{1}{2} Z \cdot C^{-1}(0) \cdot Z\right] \quad (4.63)$$

which follows from the limits,

$$\lim_{t \rightarrow \infty} C(t) = 0 \Rightarrow \lim_{t \rightarrow \infty} M(t) = C(0) \quad (4.64)$$

and, $\lim_{t \rightarrow \infty} G(t) = 0$. Thus, as expected, because the driving process was Gaussian and the equations linear, the distribution of fluctuations is also Gaussian. Furthermore, eq. (4.63) shows that the same asymptotic stationary state is reached regardless of the initial condition.

All of these results could have been obtained if we had worked with the Fokker-Planck equation rather than the fluctuation equation. For completeness, we write down the Fokker-Planck equation for $P(Z, t)$ which is easily obtained. For example, by differentiating (4.62) with respect to time,

$$\frac{\partial}{\partial t} P(Z, t) = - \sum_{\alpha, \underline{k}} \frac{\partial}{\partial Z_{\alpha}(\underline{k})} [J_{0\alpha}(Z, t) + J_{1\alpha}(Z, t)] \quad (4.65)$$

where the drift term is

$$J_{0\alpha}(Z, t) = [a_{ij} k_i \frac{\partial}{\partial t_j} Z_{\alpha}(\underline{k}) - L_{\alpha\beta}(\underline{k}, a) Z_{\beta}(\underline{k})] P(Z, t) \quad (4.66)$$

and the diffusion term is

$$J_{1\alpha}(Z,t) = \frac{1}{2} R_{\alpha\beta}(\underline{k}) \frac{\partial}{\partial Z_{\beta}(-\underline{k})} P(Z,t). \quad (4.67)$$

The matrix $R_{\alpha\beta}(\underline{k})$, the diffusion matrix, is just the correlation matrix of the stochastic forces. Equations (4.65) - (4.67) are the usual results for the relationship between a linear Langevin equation and the corresponding Fokker-Planck equation.

CHAPTER 5 NONLINEAR FLUCTUATING HYDRODYNAMICS

In this chapter, we will consider the consequences of the nonlinear terms occurring in the general fluctuating hydrodynamics model. We begin by considering a naive form of renormalization which illustrates in an intuitive way the concept of renormalization. Using this method, we will derive the lowest order renormalization of the shear viscosity explicitly deriving the nonanalytic dependence on shear rate. In the following sections, we will present a more formal development of renormalization which will result in a self-consistent formulation of the nonlinear problem. The chapter concludes with the connection between the naive and formal renormalization.

Naive Renormalization

Consider a simple, one dimensional, nonlinear, stochastic equation of the form

$$\frac{\partial}{\partial t} x + L_0 x + N_0 x^3 = f(t) \quad (5.1)$$

with a Gaussian, white stochastic source $f(t)$ having correlations,

$$\langle f(t_1) f(t_2) \rangle = f_0 \delta(t_1 - t_2) \quad (5.2)$$

and all higher order cumulants equal to zero. Furthermore, let the average of $x(t)$, $\langle x(t) \rangle$, be denoted by $x_0(t)$. Then, the equation of motion for $x_0(t)$ is found by averaging eq. (5.1),

$$\frac{\partial}{\partial t} x_0(t) + L_0 x_0(t) + N_0 \langle x^3(t) \rangle = 0. \quad (5.3)$$

If we write $x(t) = x_0(t) + \delta x(t)$, then (5.3) becomes

$$\frac{\partial}{\partial t} x_0(t) + [L_0 + 3N_0 \langle (\delta x(t))^2 \rangle] x_0(t) + N_0 x_0^3(t) = -N_0 \langle (\delta x(t))^3 \rangle. \quad (5.4)$$

We see that the equation for $x_0(t)$ has the same form as that for the fluctuating variable, $x(t)$, except that the "bare" coefficient L_0 has been renormalized by the nonlinearity to become the "dressed" or renormalized coefficient L ,

$$L = L_0 + 3N_0 \langle (\delta x(t))^2 \rangle. \quad (5.5)$$

If we subtract eq. (5.4) from (5.1) and solve the resulting equation for δx neglecting the nonlinear term, and use this to compute L , we find that

$$L = L_0 + 3N_0 f_0 / 2L_0 + o(N_0^2) \quad (5.6)$$

where we have imposed stationarity, $\frac{\partial}{\partial t} \langle x(t)x(t) \rangle = 0$, to fix the equal time correlation functions.

The previous calculation can be reformulated in terms of correlation functions. The equation of motion for the two-point function, $\langle \delta x(t) \delta x(0) \rangle = C(t)$, is found from (5.1) to be

$$\frac{\partial}{\partial t} C(t) + L_0 C(t) + N_0 \langle (\delta x(t))^3 \delta x(0) \rangle = 0 \quad (5.7)$$

where we have used the condition $\langle f(t) \delta x(0) \rangle = 0$. To lowest, $N_0 = 0$, order, we find that the Laplace transform of $C(t)$, $\tilde{C}(z)$, is

$$\tilde{C}(z) = C(0)/(-z + L_0) + o(N_0) \quad (5.8)$$

which has a pole at the bare transport coefficient L_0 . If we calculate the correlation function in (5.7) to lowest order, we find that

$$\begin{aligned} \langle (\delta x(t))^3 \delta x(0) \rangle &= \int_{-\infty}^t d\tau_1 d\tau_2 d\tau_3 \int_{-\infty}^0 d\tau_4 e^{-L_0(t-\tau_1)} e^{-L_0(t-\tau_2)} e^{-L_0(t-\tau_3)} e^{L_0\tau_4} \\ &\quad \langle f(\tau_1) f(\tau_2) f(\tau_3) f(\tau_4) \rangle + o(N_0) \\ &= 3 \int_{-\infty}^t d\tau_1 \int_{-\infty}^0 d\tau_2 e^{-2L_0(t-\tau_1)} e^{-L_0(t-\tau_2)} f_0^2 + o(N_0) \\ &= 3 \frac{1}{2L_0} \frac{1}{2L_0} e^{-L_0 t} f_0^2 + o(N_0) \\ &= \frac{3f_0}{2L_0} C^{(0)}(t) + o(N_0). \end{aligned} \quad (5.9)$$

So,

$$\frac{\partial}{\partial t} C(t) + (L_0 + \frac{3}{2} \frac{N_0 f_0}{L_0}) C(t) = o(N_0^2) \quad (5.10)$$

and

$$\tilde{C}(z) = C(0)/(-z + L_0 + \frac{3}{2} N_0 f_0 / L_0) + o(N_0^2) \quad (5.11)$$

which has a pole at the "renormalized" coefficient defined in (5.5). This coincidence is easy to understand. Suppose that at time $t=0$, the distribution function, $\rho(x)$, is perturbed from the steady state function, ρ_s , in the following way

$$\rho(t=0) = \rho_s e^{-h\delta x}. \quad (5.12)$$

The auxillary field, h , might be chosen such that

$\langle x(0) \rangle_h \neq \langle x(0) \rangle_{ss} = x_0$, i.e., to yield some particular initial value for the macroscopic variable. For small deviations from the steady state (i.e., h small so $\langle x(0) \rangle_h - \langle x(0) \rangle_{ss}$ is small), we find that

$$\begin{aligned} \langle x(t) \rangle - x_0 &= C(t)h + o(h^2) \\ &= (C(t)/C(0))[\langle x(0) \rangle_h - x_0] + o(h^2). \end{aligned} \quad (5.13)$$

Thus, the correlation function acts as the Green's function for small

deviations of the macroscopic variables. They must, therefore, share the same linear relaxation times. A general proof of this property for Markovian processes has been given by Dufty et al.⁴⁵

In the same way, we can derive an expression for the renormalized shear viscosity. If we take the average of eqs. (2.45), we require that we obtain the macroscopic hydrodynamic equations. For shear flow, the only nontrivial equation is the heat equation,

$$\frac{\partial}{\partial t} e - \eta_R a^2 = 0 \quad (5.14)$$

where η_R is the renormalized viscosity. Comparing (5.14) with the average of eqs. (2.45) yields

$$\begin{aligned} \eta_R &= -a^{-2} \langle t_{ij}(\underline{r}, t) \frac{\partial}{\partial r_j} u_i(\underline{r}, t) \rangle \\ &= a^{-2} \langle u_i(\underline{r}, t) \frac{\partial}{\partial r_j} t_{ij}(\underline{r}, t) \rangle \\ &= a^{-2} \langle u_i(\underline{r}, t) \frac{\partial}{\partial r_j} [\rho(\underline{r}, t) u_i(\underline{r}, t) u_j(\underline{r}, t)] \rangle \\ &= a^{-2} \langle \left[\frac{\partial}{\partial r_j} u_i(\underline{r}, t) \right] \rho(\underline{r}, t) u_i(\underline{r}, t) u_j(\underline{r}, t) \rangle \end{aligned} \quad (5.15)$$

where we have used temporal and spatial translational invariance to set overall derivatives of the correlation functions to zero. The third line of (5.15) follows directly from the momentum equation.

Using our results from the previous chapter, eq. (5.15) can be written, to lowest order in the nonlinearity, in terms of the equal

time correlation functions,

$$\begin{aligned}\eta_R &= a^{-1} \rho_0 \langle u_x(\underline{r}, t) u_y(\underline{r}, t) \rangle \\ &= -(2\pi)^{-6} \int d^3k [\hat{k}_x \hat{k}_y c_{33}(\underline{k}; a) + \hat{k}_x \hat{k}_y c_{44}(\underline{k}; a) - \hat{k}_z c_{45}(\underline{k}; a)].\end{aligned}\quad (5.16)$$

This equation for the lowest order renormalization of the viscosity is an example of mode coupling. That is, the original nonlinearities in the equations of motion have coupled two different hydrodynamic modes, analogous to phonons in solid state physics, and the correction to the viscosity is due to the interaction of these modes, analogous to the phonon-phonon scattering contribution to the coefficient of thermal diffusion in solids. The coupling of the modes in (5.16) is buried in the equal time correlation functions. It can be seen by referring to eq. (4.38). Contributions also exist due to three mode coupling, four mode coupling, etc.

Upon evaluation, we find that

$$\eta_R = \eta_0 + \eta_1 a^{1/2} \quad (5.17)$$

with

$$\eta_1 = -10^{-3} k_B T_0 \left[\frac{2.56}{(2\nu_0)^{3/2}} + \frac{4.17}{(\Gamma_0)^{3/2}} \right]. \quad (5.18)$$

Thus, it is seen that a nonanalytic dependence of the viscosity on shear rate arises as a result of mode coupling. This is in contrast to the analytic dependence one would obtain from the standard Chapman-Enskog solution of the Boltzmann equation (or the Enskog equation; see

Chapter 6). This result agrees with that of Ernst et al.¹⁶ and with that of Yamada and Kawasaki¹⁶ (although their numerical evaluations are incorrect). Thus, this result indicates the equivalence, with the present assumptions, of this model and the others appearing in the literature.

Formal Renormalization

In this section, we wish to develop a more general method of renormalization than the naive scheme, allowing the calculation of all renormalized properties. To this end, we begin by formulating the nonlinear model in a more general notation,

$$\frac{\partial}{\partial t} y_m + v_m[y] + D_{mn}[y]F_n[y] = M_{mn}[y]\xi_n \quad (5.19)$$

where $v_m[z]$ represents the nonlinear Euler terms in eq. (3.23) (i.e., the terms $\underline{v} \cdot \underline{j} = \underline{v} \cdot (\rho \underline{u})$ in (3.23) and ev_α and $v_\alpha j_\beta$ in (3.24)). The matrix $D_{mn}[y]$ is called the diffusion matrix and $F_n[y]$ are the thermodynamic forces which are the variables thermodynamically conjugate to the y_m 's. The product $D_{mn}F_n$ represents the dissipative terms in (3.24). The reason for returning this form of the equations is that in their derivation of fluctuating hydrodynamics, Zubarev and Morozov⁵ show that thermodynamic consistency imposes the fluctuation-dissipation theorem,

$$D_{mn}[y] = M_{mm}[y] M_{nn}[y] \Lambda_{m'n'}; \quad (5.20)$$

"thermodynamic consistency" meaning that the equilibrium distribution function is a solution to (5.17).

Equation (5.17) is highly nonlinear making a general analysis difficult. However, in equilibrium it has been found that truncating eq. (5.17) at second order in the nonlinearities provides a qualitatively correct description of such nonlinear phenomena as long time tails (i.e., the algebraic decay of equilibrium correlation functions). In fact, in equilibrium, the dominant mode coupling effects arise from the Euler terms in (5.19). We shall, therefore, consider only these nonlinearities in the rest of the discussion. It can be shown that, to order (ak) , this is equivalent to taking both D_{mn} and M_{mn} to lowest order (i.e., $D_{mn}[y] \sim D_{mn}[y_0]$) thus preserving the fluctuation-dissipation theorem, eq. (5.20), in this truncated model of eq. (5.19). Furthermore, $F_n[y]$ is expanded to first order in the fluctuations in order to preserve the usual linearized transport laws.

With these approximations, and expanding the variables y_m about their steady state averages y_{0m} , eq. (5.19) takes the form,

$$\begin{aligned} \frac{\partial}{\partial t} z_a(\underline{k}, t) + L_{ab}(\underline{k}, t) z_b(\underline{k}, t) + \epsilon V_{abc}(\underline{k}, \underline{k}_1, \underline{k}_2) (z_b(\underline{k}_1, t) z_c(\underline{k}_2, t) \\ - \langle z_b(\underline{k}_1, t) z_c(\underline{k}_2, t) \rangle) \\ = R_a(\underline{k}, t) \end{aligned} \quad (5.21)$$

where $L_{ab} = -a_{ij} k_i \frac{\partial}{\partial k_j} + H_{ab}(\underline{k}; a)$ is the linear operator studied in

the previous chapter and $z_a = y_a = y_{0a}$ (details are given in Appendix B). The vertices, which arise solely from the Euler terms, have the form

$$V_{abc}(\underline{k}, \underline{k}_1, \underline{k}_2) = A_{abc}(\underline{k}, \underline{k}_1) \delta(\underline{k} - \underline{k}_1 - \underline{k}_2) \quad (5.22)$$

where the explicit form of $A_{abc}(\underline{k}, \underline{q})$ is given in Appendix B. The constant ϵ is introduced as a notational convenience in the development of a perturbative expansion in the nonlinearity.

Equation (5.21) can be rewritten using the Green's function introduced in Chapter 4 as

$$z_a(\underline{k}; t) = z_a^{(0)}(\underline{k}; t) + \epsilon \int_0^t d\tau \{ G_{aa}(\underline{k}, \underline{q}_1; t - \tau) V_{a,bc}(\underline{q}_1, \underline{q}_2, \underline{q}_3) \\ \times (z_b(\underline{q}_2, \tau) z_c(\underline{q}_3, \tau) - \langle z_b(\underline{q}_2, 0) z_c(\underline{q}_3, 0) \rangle) \} \quad (5.23)$$

where a sum over repeated wavevectors is implicit and where

$$z_a^{(0)}(\underline{k}; t) = G_{aa}(\underline{k}, \underline{q}; t) z_a(\underline{q}, 0) + \int_0^t d\tau G_{aa}(\underline{k}, \underline{q}; t - \tau) R_a(\underline{q}, \tau). \quad (5.24)$$

Using (5.23), a perturbative solution to eq. (5.21) is easily constructed.

From eq. (5.21), we can immediately construct the equations of motion of the two-point correlation functions,

$$C_{ab}(\underline{k}, \underline{k}'; t) = \langle z_a(\underline{k}, t) z_b(\underline{k}', 0) \rangle,$$

$$\frac{\partial}{\partial t} C_{ab}(\underline{k}, \underline{k}'; t) + L_{aa}(\underline{k}; a) C_{a,b}(\underline{k}, \underline{k}'; t) + M_{ab}(\underline{k}, \underline{k}'; t) = 0 \quad (5.25)$$

where we have defined

$$M_{ab}(\underline{k}, \underline{k}'; t) = V_{acd}(\underline{k}, \underline{q}_1, \underline{q}_2) \langle z_c(\underline{q}_1, t) z_d(\underline{q}_2, t) z_b(\underline{k}', 0) \rangle \quad (5.26)$$

and have used the fact that $\langle R_a(\underline{k}, t) z_b(\underline{k}', t') \rangle = 0$ for $t' < t$ (causality--the source at time t cannot affect a fluctuation occurring at an earlier time). The process of renormalization occurs when we define a self-energy (memory function) $\bar{L}_{ab}(\underline{k}, \underline{k}'; t)$ as

$$M_{a,b}(\underline{k}, \underline{k}'; t) = \int_0^t d\tau \bar{L}_{aa}(\underline{k}, \underline{k}_1; t-\tau) C_{a,b}(\underline{k}_1, \underline{k}'; \tau). \quad (5.27)$$

The significance of this is that eq. (5.24) becomes a linear equation for the correlation functions and effective viscosities, etc. as would be measured in the laboratory may be identified.

Laplace transforming (5.24) in conjunction with (5.27), one obtains

$$\begin{aligned} z \bar{C}_{ab}(\underline{k}, \underline{k}'; w) + L_{aa}(\underline{k}; a) \bar{C}_{a,b}(\underline{k}, \underline{k}'; w) + \epsilon \bar{L}_{aa}(\underline{k}, \underline{k}_1; w) \bar{C}_{a,b}(\underline{k}_1, \underline{k}'; w) \\ = C_{ab}(\underline{k}, \underline{k}'; t=0) \end{aligned} \quad (5.28)$$

and the Fourier transformed self-energy may be computed from (5.27),

$$\tilde{\Sigma}_{ab}(\underline{k}, \underline{k}_1; w) = \tilde{M}_{ac}(\underline{k}, \underline{q}; w) \tilde{C}_{cb}^{-1}(\underline{q}, \underline{k}_1; w). \quad (5.29)$$

As discussed in the previous chapter, $C_{ab}(\underline{k}, \underline{k}'; t) = C_{ab}(\underline{k}, t) \delta(\underline{k} - \underline{k}'(t))$ and it is easily verified that, order by order in perturbation theory,

$M_{ab}(\underline{k}, \underline{k}'; t) = M_{ab}(\underline{k}, t) \delta(\underline{k} - \underline{k}'(t))$ which requires that

$\Sigma_{ab}(\underline{k}, \underline{k}', t) = \Sigma_{ab}(\underline{k}, t) \delta(\underline{k} - \underline{k}'(t))$. Thus, eq. (5.28) becomes

$$\frac{\partial}{\partial t} C_{ab}(\underline{k}, t) + D(\underline{k}) C_{ab}(\underline{k}, t) + H_{aa},(\underline{k}; a) C_{a,b}(\underline{k}, t) + \epsilon M_{ab}(\underline{k}, t) = 0 \quad (5.30)$$

where we have introduced $D = -a_{ij} k_i \frac{\partial}{\partial k_j}$. The equation for the self-energy becomes

$$\begin{aligned} M_{ab}(\underline{k}, t) &= \int_0^t d\tau \Sigma_{aa},(\underline{k}; t-\tau) C_{a,b}(\underline{k}(\tau-t), \tau) \\ &= \int_0^t d\tau \Sigma_{aa},(\underline{k}; t-\tau) e^{-D(t-\tau)} C_{a,b}(\underline{k}, \tau) \end{aligned} \quad (5.31)$$

which shows the self-energy to be an operator in k -space. Laplace transforming (5.31) yields an expression for the self-energy,

$$\begin{aligned} \int_0^\infty dt e^{-wt} \Sigma_{aa},(\underline{k}; t) e^{-Dt} &= \tilde{M}_{ab}(\underline{k}; w) \tilde{C}_{ba}^{-1}(\underline{k}; w). \\ &= \tilde{\Sigma}_{aa},(\underline{k}, w) \end{aligned} \quad (5.32)$$

and the Laplace transform of (5.30) is

$$\begin{aligned}
 [w+D]\tilde{C}_{ab}(\underline{k},w) + H_{aa}(\underline{k},a)\tilde{C}_{a'b}(\underline{k},w) + \varepsilon \int_0^\infty dt \sum_{aa'}(\underline{k};(\tau))e^{-(w+D)(\tau)}\tilde{C}_{a'b}(\underline{k},w) \\
 = C_{ab}(\underline{k},t=0).
 \end{aligned}
 \tag{5.33}$$

Equations (5.32) and (5.33) are the primary results of this section. The linear mode coupling which was the unique feature of the linear problem is seen to play an important role here as well. The operator nature of the self-energy is a result of the linear mode coupling and expresses the fact that new gradient couplings, as well as the expected new hydrodynamic couplings, arise as a result of the process of renormalization. This complication is, however, removed in the context of perturbation theory in ε because we have an expression, to lowest order in ε , for the operator $(w+D)$ acting on the correlation functions (c.f. eq. (5.33)). It is seen that the self-energy function shifts the poles of the correlation function renormalizing the transport coefficients as in eq. (5.11).

Application of Formal Renormalization

We now wish to apply the renormalization formalism to the calculation of the renormalized shear viscosity and, in so doing, to make a connection with the naive renormalization method. As a simplification, we will restrict our attention to the contribution arising from the shear modes. In this case, the irreversible part of the stress tensor, t_{ij}^* , can, in general, be written as

$$t_{ij}^* = v_{ijlm} \frac{\partial}{\partial r_l} j_m \quad (5.34)$$

where v_{ijlm} is the viscosity tensor which, in the unrenormalized theory, has the Navier-Stokes form,

$$v_{ijlm} = v(\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl} - \frac{2}{3}\delta_{ij}\delta_{lm}) + \kappa\delta_{ij}\delta_{lm} \quad (5.35)$$

where v and κ are the usual kinematic and bulk viscosities, respectively. The macroscopic equation for the energy density is

$$\frac{\partial}{\partial t} e + \frac{\partial}{\partial r_i} [(e + p)\rho_0^{-1} j_i + t_{il}\rho_0^{-1} j_l + s_i] = 0 \quad (5.36)$$

For macroscopic shear flow, using eq. (5.34), the heating equation becomes

$$\frac{\partial}{\partial t} e + v_{ijlm} a_{ij} a_{lm} = 0. \quad (5.37)$$

Thus, the renormalized viscosity calculated earlier from the heating equation corresponds to the $yxyx$ element of the general viscosity tensor.

We now calculate the self-energy to second order in the nonlinearity (i.e., to second order in ϵ). Using eqs. (5.23) and (5.26), we find that

$$\begin{aligned}
M_{ab}(\underline{k}, \underline{k}'; t) = & \epsilon V_{acd}(\underline{k}, q_1, q_2) \langle z_c^{(0)}(q_1, t) z_d^{(0)}(q_2, t) z_b(\underline{k}', 0) \rangle \\
& + 2\epsilon^2 \int_0^t d\tau \{ V_{acd}(\underline{k}, q_1, q_2) G_{ce}(q_1, q_3; t-\tau) V_{efg}(q_3, q_4, q_5) \\
& \times \langle z_f^{(0)}(q_4, \tau) z_g^{(0)}(q_5, \tau) z_d^{(0)}(q_2, \tau) z_b(\underline{k}', 0) \rangle \} + o(\epsilon^3)
\end{aligned}
\tag{5.38}$$

where the factor of two arises from the symmetry of the vertices.

Using eq. (5.24) and causality, this reduces to

$$\begin{aligned}
M_{ab}(\underline{k}, \underline{k}'; t) = & \epsilon V_{acd}(\underline{k}, q_1, q_2) G_{cc'}(q_1, q_3; t) G_{dd'}(q_2, q_4; t) \\
& \times \langle z_{c'}(q_3, 0) z_{d'}(q_4, 0) z_b(\underline{k}', 0) \rangle \\
& + 2\epsilon^2 \int_0^t d\tau \{ V_{acd}(\underline{k}, q_1, q_2) G_{ce}(q_1, q_3; t-\tau) V_{efg}(q_3, q_4, q_5) \\
& G_{ff'}(q_4, q_4'; \tau) G_{gg'}(q_5, q_5'; \tau) G_{dd'}(q_2, q_2'; t) \\
& \times \langle z_f(q_4, 0) z_g(q_5, 0) z_{d'}(q_2, 0) z_b(\underline{k}', 0) \rangle \} + o(\epsilon^3).
\end{aligned}
\tag{5.39}$$

In equilibrium, the equal time fluctuations are Gaussian distributed making the $o(\epsilon)$ term in eq. (5.39) zero and allowing easy evaluation of the $o(\epsilon^2)$ term. In the steady-state, the equal time fluctuations are not necessarily Gaussian distributed. Stationarity, in the steady state, allows us to write

$$z_a(\underline{k};0) = z_a^{(0)}(\underline{k};0) + \epsilon \int_{-\infty}^0 d\tau \{ G_{aa'}(\underline{k}, \underline{q}_1, -\tau) V_{a'bc}(\underline{q}_1, \underline{q}_2, \underline{q}_3) \\ \times (z_b(\underline{q}_2; \tau) z_c(\underline{q}_3; \tau) - \langle z_b(\underline{q}_2; \tau) z_c(\underline{q}_3; \tau) \rangle) \} \quad (5.40)$$

where

$$z_a^{(0)}(\underline{k};0) = \int_{-\infty}^0 d\tau G_{aa'}(\underline{k}, \underline{q}; -\tau) R_a(\underline{q}_1 - \tau) \quad (5.41)$$

and

$$z_a^{(0)}(\underline{k}, -t) = \int_{-\infty}^{-t} d\tau G_{aa'}(\underline{k}, \underline{q}; -t - \tau) R_a(\underline{q}_1 - \tau) \quad (5.42)$$

where in (5.42), $t > 0$. Thus, the equal time fluctuations may be determined perturbatively and are Gaussian distributed to zeroth order in ϵ .

Equations (5.39) - (5.42) provide us with enough information to calculate the self-energy function from eq. (5.28). The result is that

$$\tilde{\Sigma}_{aa'}(\underline{k}, \underline{k}''; \omega) = \epsilon \int_0^\infty dt e^{-i\omega t} \{ V_{acd}(\underline{k}, \underline{q}_1, \underline{q}_2) G_{cc'}(\underline{q}_1, \underline{q}_3; t) G_{dd'}(\underline{q}_2, \underline{q}_4; t) \\ \times \langle z_c(\underline{q}_3, 0) z_{d'}(\underline{q}_4, 0) z_b(\underline{k}', 0) \rangle \} \tilde{C}_{ba'}^{(0)-1}(\underline{k}', \underline{k}''; z)$$

$$\begin{aligned}
& + 4\epsilon^2 \int_0^\infty dt e^{-wt} \{ v_{acd}(\underline{k}, q_1, q_2) v_{ega}(\underline{q}_3, q_4, \underline{k}'') \\
& \quad \times G_{de}(\underline{q}_2, q_3; t) G_{cd}(\underline{q}_1, q_2'; t) \} \langle z_d(\underline{q}_2', 0) z_g(\underline{q}_4, 0) \rangle \\
& + o(\epsilon^3).
\end{aligned} \tag{5.43}$$

To recover our previously calculated lowest order mode coupling contribution to the viscosity, we first replace the equal-time correlations in (5.43) with their local equilibrium values. The term proportional to ϵ in (5.43) then vanishes and (5.43) becomes

$$\begin{aligned}
\tilde{\Sigma}_{aa}(\underline{k}, \underline{k}''; w) &= \frac{k_B T_0}{\rho_0} \int_0^\infty dt e^{-wt} \{ A_{acd}(\underline{k}, q) A_{eya}(\underline{k}(-t) - \underline{q}(-t), -\underline{q}(-t)) \\
& \quad \times G_{de}(\underline{k} - \underline{q}; t) G_{cd}(\underline{q}; t) e^{-D(\underline{k})t} \} \delta(\underline{k} + \underline{k}'').
\end{aligned} \tag{5.44}$$

The momentum-momentum self-energy upon evaluation is found to have the form

$$\tilde{\Sigma}_{pp}(\underline{k}, z) = k_i k_j \tilde{\Sigma}_{ijpp}(\underline{k}, z) \tag{5.45}$$

which identifies it as the renormalization of the viscosity tensor.

If we write $v_{ijlm} = v_{ijlm}^{(0)} + \delta v'_{ijlm}$, then the long wavelength, long time hydrodynamic viscosity appearing in eq. (5.37) is

$$\delta v_{yxy} = \lim_{\substack{k \rightarrow 0 \\ w \rightarrow 0}} \tilde{\sum}_{yxp_y} (k, w) \quad (5.46)$$

from which the "naive" result is recovered.

The replacement of the static correlation functions by their local equilibrium values requires some comment. For a stationary process, the correlation of the stochastic sources is related through fluctuation-dissipation theorems to the static correlations. The mode coupling contributions to the static correlations may thus be interpreted as a renormalization of the amplitudes of the stochastic sources. By neglecting the equal time three-point function in (5.42), we were left with the propagator renormalization.

There is another way to understand the replacement of the static correlations in the present calculation by their local equilibrium values in order to find agreement with the "naive" calculation. The only information about the "statics" that was used in the "naive" calculation was the stochastic source correlations. But, as explained in Chapter 3, these are approximated, in the unrenormalized theory, by their local equilibrium values. It is, therefore, reasonable that the same information must be used in both calculations to obtain agreement. We speculate that if the first order renormalized forces were used in the naive calculation, one would obtain the same result as is obtained here without the local equilibrium replacement.

CHAPTER 6

SHORT TIME MODEL

In this chapter, we discuss the explicit form of the short time model of hydrodynamic fluctuations introduced in Chapter 3. We recall that this model is intended to describe hydrodynamic fluctuations on length scales as small as atomic lengths. We begin by discussing general properties of the distribution functions. This is followed by a derivation of explicit expressions for the necessary matrix elements in terms of the reduced distribution functions. The final two sections describe the approximations introduced to evaluate these matrix elements and the explicit form of the resulting equations governing the time evolution of hydrodynamic fluctuations.

General Properties of the Reduced Distribution Functions

In this section, we introduce two properties of the distribution functions which will be of use in determining the general nature of the expressions, eqs. (3.31)-(3.34), to be evaluated below and which will aid in their evaluation. These properties are the stationarity, in time, and the modified translational invariance of the distribution functions.

As discussed in Chapter 2, an external nonconservative force is applied in computer simulations of sheared fluids to counterbalance viscous heating of the system. The significance of this is that it

yields a steady state. If we denote by $\rho_{ss}(\Gamma)$ the distribution function (density matrix) of the steady state system, depending on all of the phase space variables $\Gamma = \{q_i, p_i\}_{i=1}^N$, then we can write the steady state Liouville equation as

$$0 = \frac{\partial}{\partial t} \rho_{ss}(\Gamma) + \hat{\mathcal{L}}_- \rho(\Gamma) \quad (6.1)$$

$$= \hat{\mathcal{L}}_- \rho(\Gamma) \quad (6.2)$$

where $\hat{\mathcal{L}}_-$ is the Liouville operator. The explicit form of $\hat{\mathcal{L}}_-$ is generally given by

$$\hat{\mathcal{L}}_- = \sum_{n=1}^N \frac{1}{m} p_n \cdot \frac{\partial}{\partial q_n} - \frac{1}{2} \sum_{n \neq n'} \frac{\partial V(|q_n - q_{n'}|)}{\partial q_n} \cdot \frac{\partial}{\partial p_n} + \hat{\mathcal{L}}_{\text{ext}} \quad (6.3)$$

where $V(|q_n - q_{n'}|)$ is the pair potential. For hard spheres, the potential is singular rendering eq. (6.3) ill defined. As discussed in Chapter 3, however, eq. (6.3) can be replaced by a well defined expression which produces a statistically equivalent dynamical system

$$\hat{\mathcal{L}}_- = \sum_{n=1}^N p_n \cdot \frac{\partial}{\partial q_n} + \frac{1}{2} \sum_{n \neq n'} [\bar{T}_-(n, n') + \bar{T}_-(n', n)] + \hat{\mathcal{L}}_{\text{ext}} \quad (6.4)$$

where we have included a term representing the externally applied thermostat alluded to above. The explicit form of the T operator and its various adjoints and time-reversed forms are given in the literature and will not be repeated here. The point we wish to make

is that (6.2) allows the $\hat{\mathcal{L}}_+$ operator to be moved in averages, i.e., for any two phase functions, $\hat{A}(\Gamma)$ and $\hat{B}(\Gamma)$, it can be shown that

$$\langle \hat{A}(\Gamma)(\hat{\mathcal{L}}_+ \hat{B}(\Gamma)) \rangle_{ss} = \langle (\hat{\mathcal{L}}_- \hat{A}(\Gamma)) \hat{B}(\Gamma) \rangle_{ss}. \quad (6.5)$$

The subscript on $\mathcal{L}_-$ refers to the fact that T_+ goes to its time reversed form T_- .

Another important property of the distribution functions is their modified translational invariance. Clearly, because the local flow velocity varies spatially, the distribution function cannot be translationally invariant. That is, if

$$p_i, q_i \rightarrow p_i^*, q_i^* - \underline{R} \quad (6.6)$$

for an arbitrary displacement $\underline{R}$, then

$$\rho_{ss}(\Gamma) = \rho_{ss}(\Gamma^*). \quad (6.7)$$

However, if we make the transformation

$$p_i, q_i \rightarrow p_i^* - m a_{ij} R_j, \quad q_i^* - \underline{R}, \quad (6.8)$$

then we expect the distribution function to be invariant since the macroscopic state is characterized by the local velocity and the local velocity gradient and, while (6.6) does not preserve these properties, (6.8) does. Mathematically, it is easy to verify that (6.8) is

consistent with the Lees-Edwards boundary conditions while (6.6) is not. We, therefore, look for solutions of Liouville's equation which are functions of the variables

$$\begin{aligned} p'_i &= p_i - m a_{ij} q_j \\ q_{ij} &= q_i - q_j \end{aligned} \quad (6.9)$$

which are invariant under (6.8),

$$p'_i, q_i \rightarrow p_i^*, q_{ij}^*. \quad (6.10)$$

Henceforth, we will write $\rho_{ss}(\Gamma) = \rho_{ss}(\{p'_i, q_{ij}\})$.

Explicit Form of Matrix Elements

The short time model is given in Chapter 3 as

$$\frac{\partial}{\partial t} \tilde{y}_\alpha(\underline{k}, t) + L_{\alpha\beta}(\underline{k}, \underline{k}'; a) \delta \tilde{y}_\beta(\underline{k}', t) = 0 \quad (6.11)$$

where

$$L_{\alpha\beta}(\underline{k}, \underline{k}'; a) = \langle (\hat{\mathcal{L}}_+ \hat{y}_\alpha(\underline{k})) \delta \hat{y}_\gamma(\underline{k}'') \rangle_{ss} (g^{-1})_{\gamma\beta, \underline{k}'', \underline{k}'} \quad (6.12)$$

and

$$g_{\gamma\beta}(\underline{k}'') = \langle \hat{\delta y}_{\gamma}(\underline{k}'') \hat{\delta y}_{\beta}(\underline{k}') \rangle_{ss}. \quad (6.13)$$

The variables, $\hat{\delta y}_{\alpha}(\underline{k})$, are again taken to be the fluctuations of the conserved densities around the steady state:

$$\begin{aligned} \hat{\delta y}_1(\underline{k}) &= \hat{\rho}(\underline{k}) = \frac{1}{\sqrt{V}} \sum_n m e^{i\underline{k} \cdot \underline{q}_n} \\ \hat{\delta y}_2(\underline{k}) &= \hat{\delta e}'(\underline{k}) = \frac{1}{\sqrt{V}} \sum_n \left(\frac{p_n'^2}{2m} - \frac{3}{2} k_B T_0 \right) e^{i\underline{k} \cdot \underline{q}_n} \\ \hat{\delta y}_{2+\beta}(\underline{k}) &= \hat{\delta j}_{\beta}'(\underline{k}) = \frac{1}{\sqrt{V}} \sum_n (p_n')_{\beta} e^{i\underline{k} \cdot \underline{q}_n} \end{aligned} \quad (6.14)$$

which are summarized as

$$\hat{\delta y}_{\alpha}(\underline{k}) = \frac{1}{\sqrt{V}} \sum_n \hat{Y}_{\alpha}(p_n') e^{i\underline{k} \cdot \underline{q}_n}, \quad (6.15)$$

where V is the volume of the system.

We now define the reduced distribution functions,

$$n_f^{(n)}(X_1', \dots, X_n') = \frac{N!}{(N-n)!} \int dX_{n+1}' \dots dX_n' \rho_{ss}(\Gamma') \quad (6.16)$$

where $X_n' \leftrightarrow (\underline{q}_n, p_n')$ and we note that the Jacobian of the change of variables $X_n' \leftrightarrow X_n'$ is unity. Using (6.16) and the independence of ρ_{ss} on the center of mass, we find that

$$g_{\alpha\beta}(\underline{k}, \underline{k}') = (2\pi)^3 V^{-1} \delta(\underline{k} + \underline{k}') g_{\alpha\beta}(\underline{k}), \quad (6.17)$$

where

$$\begin{aligned}
 g_{\alpha\beta}(\underline{k}) = & n \int d\underline{p}'_1 f^{(1)}(\underline{p}'_1) \hat{Y}_{\alpha}(\underline{p}'_1) \hat{Y}_{\beta}(\underline{p}'_1) \\
 & + \frac{1}{2} n^2 \int d\underline{p}'_1 d\underline{p}'_2 d\underline{r}_{12} f^{(2)}(\underline{p}'_1, \underline{p}'_2, \underline{r}_{12}) \hat{Y}_{\alpha}(\underline{p}'_1) \hat{Y}_{\beta}(\underline{p}'_2) e^{i\underline{k} \cdot \underline{r}_{12}}.
 \end{aligned} \quad (6.18)$$

The explicit form of $\hat{\underline{x}}_+ \hat{y}_{\alpha}(\underline{k})$ is easily found to be

$$\begin{aligned}
 \hat{\underline{x}}_+ \hat{y}_{\alpha}(\underline{k}) = & i \frac{1}{\sqrt{v}} \sum_n \underline{k} \cdot \frac{\underline{p}'_n}{m} \hat{Y}_{\alpha}(\underline{p}'_n) e^{i\underline{k} \cdot \underline{q}_n} \\
 & + \frac{1}{2} \frac{1}{\sqrt{v}} \sum_{n \neq n'} [T_+(n, n') + T_+(n', n)] \hat{Y}_{\alpha}(\underline{p}'_n) e^{i\underline{k} \cdot \underline{q}_n} \\
 & - k_i a_{ij} \frac{\partial}{\partial k_j} \hat{y}_{\alpha}(\underline{k}) + \hat{\underline{x}}_{\text{ext}} \hat{y}_{\alpha}(\underline{k}).
 \end{aligned} \quad (6.19)$$

From this, it follows that

$$\begin{aligned}
 \langle (\hat{\underline{x}}_+ \hat{y}_{\alpha}(\underline{k})) \delta \hat{y}_{\beta}(\underline{k}') \rangle_{ss} = & (2\pi)^3 \delta(\underline{k} + \underline{k}') M_{\alpha\beta}(\underline{k}) \\
 & - k_i a_{ij} \frac{\partial}{\partial k_j} \langle \hat{y}_{\alpha}(\underline{k}) \hat{y}_{\beta}(\underline{k}') \rangle_{ss} \\
 & + \langle (\hat{\underline{x}}_{\text{ext}} \hat{y}_{\alpha}(\underline{k})) \hat{y}_{\beta}(\underline{k}') \rangle_{ss},
 \end{aligned} \quad (6.20)$$

where

$$\begin{aligned}
M_{\alpha\beta}(\underline{k}) = & i n \underline{k} \cdot \int d\underline{p}_1' \frac{\underline{p}_1'}{m} \hat{Y}_{\alpha}(\underline{p}_1') \hat{Y}_{\beta}(\underline{p}_1') f^{(1)}(\underline{p}_1') \\
& + i \frac{n^2}{2} \underline{k} \cdot \int d\underline{p}_1' d\underline{p}_2' d\underline{q}_{12} \frac{\underline{p}_1'}{m} \hat{Y}_{\alpha}(\underline{p}_1') \hat{Y}_{\beta}(\underline{p}_2') f^{(2)}(\underline{p}_1', \underline{p}_2'; \underline{q}_{12}) \\
& + \frac{1}{2} n^2 \int d\underline{p}_1' d\underline{p}_2' d\underline{q}_{12} ([T_+(1,2) + T_+(2,1)]) \hat{Y}_{\alpha}(\underline{p}_1') \hat{Y}_{\beta}(\underline{p}_1') f^{(2)}(\underline{p}_1', \underline{p}_2'; \underline{q}_{12}) \\
& + \frac{n^2}{2} \int d\underline{p}_1' d\underline{p}_2' d\underline{q}_{12} ([T_+(1,2) + T_+(2,1)]) \hat{Y}_{\alpha}(\underline{p}_1') \hat{Y}_{\beta}(\underline{p}_2') e^{\frac{1}{2} \underline{k} \cdot \underline{r}_{12}} \\
& \quad \times f^{(2)}(\underline{p}_1', \underline{p}_2'; \underline{q}_{12}) \\
& + \frac{n^2}{3!} \int d\underline{p}_1' d\underline{p}_2' d\underline{p}_3' d\underline{q}_{12} d\underline{q}_{13} ([T_+(1,2) + T_+(2,1)]) \hat{Y}_{\alpha}(\underline{p}_1') \hat{Y}_{\beta}(\underline{p}_3') e^{\frac{1}{2} \underline{k} \cdot \underline{r}_{13}} \\
& \quad \times f^{(3)}(\underline{p}_1', \underline{p}_2', \underline{p}_3'; \underline{q}_{12}, \underline{q}_{13}). \tag{6.21}
\end{aligned}$$

Approximations

The evaluation of eqs. (6.21) and (6.18) require knowledge of the one- and two-body reduced distribution functions for the steady state. In general, these functions cannot be determined explicitly and, so, we introduce two important approximations.

The first of these is the neglect of momentum correlations, which is to say we assume the two-body distribution to have the form

$$\begin{aligned}
f^{(2)}(\underline{x}_1', \underline{x}_2') &= f^{(2)}(\underline{p}_1', \underline{p}_2'; \underline{q}_{12}) \\
&= f^{(1)}(\underline{p}_1') f^{(1)}(\underline{p}_2') g(\underline{q}_{12}), \tag{6.22}
\end{aligned}$$

where $f^{(1)}(\underline{p}_1')$ is the one-body reduced distribution function, which cannot depend on $\underline{q}_1$ due to the modified translational invariance, and the function $g(\underline{q}_{12})$ is the steady state analogue of the pair correlation function (i.e., $g(\underline{q}_{12})d\underline{q}_{12}$ is the probability of finding a particle, 2, in the volume $d\underline{q}_{12}$ if there is a particle, 1, at position $\underline{q}_1$). In equilibrium, this approximate form becomes exact. However, away from equilibrium, we expect that particle velocities are indeed correlated (i.e., (6.22) implies that $\langle \underline{p}_1 \underline{p}_2 \rangle_{ss} = 0$ but in general this need not be the case). This approximation, which is analogous to Boltzmann's Stosszahlansatz,⁴³ is standard in the development of kinetic equations. In particular, it is used to derive the Enskog equation which is known to give a qualitatively accurate description of fluids near equilibrium.⁴³ With this approximation, the three-body term in (6.21) only contributes for $\beta=1$. In Appendix D, it is shown that this term can be written, using an exact identity following from stationarity, in terms of two-body functions.

Having adopted the form (6.22), we must still determine the one-body distribution and the pair correlation function. The second approximation we use is to replace the steady state pair correlation function, $g(\underline{q}_{12})$, by the local equilibrium pair correlation function, $g_{LE}(|\underline{q}_{12}|) = g_{LE}(\underline{q}_{12})$. The pair correlation function is related to the density-density equal time correlation function and knowledge of one of these allows determination of the other. This approximation, which, like the previous one, is used in the derivation of various kinetic equations, may be thought of as a first guess to be "renormalized" using the density autocorrelation function calculated

from the resulting equations. This approximation then becomes the first iteration of a self-consistent calculation. In fact, these two approximations require that $f^{(1)}(\underline{p}_1')$ satisfy an Enskog equation which is the usual dense fluid analogue of the Boltzmann equation.

With these approximations, our model is completely defined. The one-body distribution can be obtained from the first equation of the BBGKY hierarchy (i.e., by integrating eq. (6.2) over coordinates $X_2 \dots X_N$ and using eqs. (6.4) and (6.22)):

$$\frac{\underline{p}_1'}{m} \frac{\partial}{\partial \underline{q}_1} f^{(1)}(\underline{p}_1') = \int d\underline{x}_2 \bar{T}_-(12) f^{(1)}(\underline{p}_1) f^{(1)}(\underline{p}_2) g_{LE}(\underline{q}_{12})$$

+ sources. (6.23)

The sources in eq. (6.23) arise from the nonconservative forces in the Liouville equation (eq. 6.4). However, it can be shown that they contribute to second order in the shear rate and so are neglected in the present calculation which is only carried out to first order in the shear. While the previous approximations served to construct a model, we now make an approximation with respect to solving that model; we will only work to first order in the shear rate. Thus we expand $f^{(1)}$,

$$f^{(1)}(\underline{p}_1') = f_{LE}(\underline{p}_1') (1 + a^* \phi_1(\underline{p}_1') + \dots) \quad (6.24)$$

where $f_{LE}(\underline{p}_1')$ is the local equilibrium distribution function for uniform shear flow,

$$f_{LE}(p'_1) = n(2\pi mk_B T_0)^{-3/2} \exp - (p_1'^2/2mk_B T_0). \quad (6.25)$$

With these approximations, one is able to determine $\phi_1(p'_1)$ in eq. (6.25). As this result exists in the literature,⁴³ we only quote it here:

$$a\phi^{(1)}(p'_1) = -a_{ij}\eta_k\beta_0^2/r_0(p'_{1i}p'_{1j} - \frac{1}{3}p_1'^2\delta_{ij})$$

$$\eta_k = \frac{1}{\chi} [1 + \frac{4}{15} \pi n^* \chi] \eta_B$$

$$\eta_B = \frac{5}{16\sigma^2} (m/\pi\beta_0)^{1/2} \quad (6.26)$$

and $\chi = g_{LE}(\sigma)$. The constant, η_B , is the kinetic part of the viscosity as calculated from the Boltzmann equation. It should be noted that we have only sought the steady-state solution of eq. (6.22).

With these approximations, the matrix $g_{\alpha\beta}(\underline{k})$ may be determined to be

$$g_{11}(\underline{k}, a) = nS(k)$$

$$g_{22}(\underline{k}, a) = \frac{3}{2} n(k_B T_0)^2$$

$$g_{\alpha\beta}(\underline{k}, a) = \rho_0 k_B T_0 \delta_{\alpha\beta} - m\eta_k (a_{ij} + a_{ji}) \quad \alpha=1+2, \beta=j+2=3,4,5$$

$$g_{\alpha\beta} = 0 \quad \text{all others} \quad (6.27)$$

while the matrix $M_{\alpha\beta}(\underline{k}, a)$ can be written as

$$\begin{aligned}
 M_{\alpha\beta} = & -n \left\langle \frac{i \underline{k} \cdot \underline{p}'}{m} \hat{y}_{\alpha}(\underline{p}') \hat{y}_{\beta}(\underline{p}') \right\rangle_E \\
 & + \delta_{\alpha 2} n a_{ij} \left((p'_i p'_j - \frac{1}{3} p'^2 \delta_{ij}) / m, \hat{y}_{\beta}(\underline{p}') \right) \\
 & + I_{\alpha\beta} - S_{\alpha\beta}
 \end{aligned} \tag{6.28}$$

where $\langle \dots \rangle_E$ denotes an average over $f_E(\underline{p}')$ truncated to first order in a . The collisional contribution, $I_{\alpha\beta}$, is

$$\begin{aligned}
 I_{\alpha\beta}(\underline{k}, a) = & -n^2 \chi \int d\underline{p}'_1 d\underline{p}'_2 d\underline{q}_{12} \hat{y}_{\alpha}(\underline{p}'_1) \bar{T}_{-}(12) f^{(1)}(\underline{p}'_1) f^{(1)}(\underline{p}'_2) \\
 & \times [\hat{y}_{\beta}(\underline{p}'_1) + \hat{y}_{\beta}(\underline{p}'_2) e^{\frac{i \underline{k} \cdot \underline{q}_{12}}{m}} - \delta_{\beta 1} e^{\frac{i \underline{k} \cdot \underline{q}_{12}}{m}}]
 \end{aligned} \tag{6.29}$$

and the source term, $S_{\alpha\beta}$, is

$$S_{\alpha\beta} = \langle (\hat{f}_{\text{ext}} \hat{y}_{\alpha}(\underline{k})) [\hat{y}_{\beta}(-\underline{k}) - \langle \hat{y}_{\beta}(-\underline{k}) \rangle_{ss}] \rangle_{ss}. \tag{6.30}$$

It is shown in Appendix D that $S_{\alpha\beta} \sim a^2$, allowing us to neglect it here.

Hydrodynamic Equations

Once the various integrals have been performed, we find the following form for the short time hydrodynamic equations, where the

stars indicate dimensionless quantities with lengths scales to σ and times to t_E ,

$$D_t^{**} - i x k \cdot \underline{j}^* = 0$$

$$\begin{aligned} D_t^{**} \delta e^* + [D_T^*(x) x^2 + a^* c_1 \hat{k}_x \hat{k}_y] \delta e^* \\ - i [x h(x) \hat{k}_\alpha - a^* (c_2 + \frac{x \bar{v}^*}{6y}) (\hat{k}_y \delta_{\alpha x} + \hat{k}_x \delta_{\alpha y}) - a^* c_3 \hat{k}_x \hat{k}_y \hat{k}_\alpha] \delta j_\alpha^* \\ = o(a^2) \end{aligned}$$

$$\begin{aligned} D_t^{**} \delta j_\alpha^* - i [x P_\rho(x) \hat{k}_\alpha - a^* \frac{\bar{v}^* x}{6y S(x)} (\hat{k}_y \delta_{\alpha x} + \hat{k}_x \delta_{\alpha y})] \delta \rho^* \\ - i [x P_e(x) \hat{k}_\alpha - a^* (c_4 + \frac{8y \bar{v}^*}{\pi} x) (\hat{k}_y \delta_{\alpha x} + \hat{k}_x \delta_{\alpha y})] \delta e^* \\ + \frac{2}{3} [v^*(x) x^2 \delta_{\alpha\beta} + (v^*(x) - v^*(x)) x^2 \hat{k}_\alpha \hat{k}_\beta] \delta j_\beta^* \\ + a^* [c_6 (\delta_{\alpha x} \delta_{\beta y} + \delta_{\alpha y} \delta_{\beta x}) + c_7 \hat{k}_x \hat{k}_y \delta_{\alpha\beta} \\ + c_8 \hat{k}_\alpha (\hat{k}_y \delta_{\beta x} + \hat{k}_x \delta_{\beta y}) + c_9 (\hat{k}_y \delta_{\alpha x} + \hat{k}_x \delta_{\alpha y}) \hat{k}_\beta \\ + c_{10} \hat{k}_x \hat{k}_y \hat{k}_\alpha \hat{k}_\beta] \delta j_\beta^* + a^* \delta_{\alpha x} \delta_{\beta y} \delta j_\beta^* = o(a^2) \end{aligned} \quad (6.31)$$

where $x = k\sigma$ and,

$$D_T^*(x) = \frac{2}{3} (1 - j_0(x))/x^2$$

$$v^*(x) = \frac{2}{3} (1 - j_0(x) + 2j_2(x))/x^2$$

$$v^*(x) = \frac{2}{3} (1 - j_0(x) - j_2(x))/x^2$$

$$h^*(x) = \frac{\pi}{36y^2} (1 + 3yj_1(x)/x)$$

$$P_\rho^*(x) = \frac{\pi}{36y^2} S^{-1}(x)$$

$$P_e(x) = \frac{2}{3} (1 + 3yj_1(x)/x) \quad (6.32)$$

are wavevector dependent generalizations of the thermal conductivity, viscosity, shear viscosity, enthalpy, density derivative of pressure

and energy derivative of pressure. The constants $y = \frac{2}{3} \pi n \sigma^3 \chi$

and $\bar{v}^* = \frac{5\pi}{24y} [1 + \frac{2}{5} y]$; $\bar{v}^*$ is a dimensionless form of the kinetic contribution to the viscosity, η_k . The functions $j_n(x)$ are n^{th} -order spherical Bessel functions with $j_1(x) = (\sin x)/x$. The

functions $c_i = c_i(x; a)$ are given in Table 6.1. Finally,

$\rho^* = \rho \sigma^3$, $j^* = jt_E^2/\sigma$, etc. while $D_t^* = \frac{\partial}{\partial t^*} - a_{ij}^* k_i \frac{\partial}{\partial k_j}$ is the convective derivative in terms of dimensionless time $t^* = t/t_E$ and $a^* = at_E$.

At this point, we make a few comments about the general nature of these equations. The first of eqs. (6.31) is the familiar continuity equation describing the conservation of mass. The second two

equations describe, respectively, the conservation of energy and momentum. However, due to the fact that the effects of atomic structure are included, they are more complicated than at small wavevector. These complications disappear if we take $x \ll 1$ and expand to second order in x in which case we get a short time version of the linearized Navier-Stoke's equations. We note that in h , P_e , P_p and c_2 we have picked up second order contributions to the pressure in the long wavelength (small x) limit. To illustrate the meaning of the new couplings, we have, in Table 6.2, given the expansions of the coefficients c_i to second order in x . It is seen that all of the collisional contributions to the nonequilibrium couplings are of third order or higher in the gradients except for c_2 (recall that these coefficients are all multiplied by the shear rate, a , which is a first order gradient). Thus, they do not appear in the ordinary Navier-Stokes equations but rather in the higher order, so called Burnett, equations. They are always present in the analysis to be presented below, however, as we keep all orders in $k\sigma$.

Also, these equations contain wavevector dependent "transport coefficients," eq. (6.32), which are the high frequency limit of the general wavevector and frequency dependent transport coefficients,

$$D_T^*(x) = \lim_{\omega \rightarrow \infty} D_T(x, \omega), \quad (6.33)$$

etc. Wavevector dependent susceptibilities such as the pressure derivatives also appear. An important feature of the transport

Table 6.1 Coefficients appearing in hydrodynamic equations.

$c_1^* = -3y[1 + \frac{20}{3\pi} \bar{v}^*]j_2$	$c_2^* = \frac{2}{5} [1 + \frac{1}{2} \bar{v}^*](j_1 + j_3)$
$c_3^* = -2[1 + \frac{1}{2} \bar{v}^*]j_3$	$c_4^* = \frac{12}{5\pi} y^2[1 + 4\bar{v}^*](j_1 + j_3)$
$c_5^* = -\frac{12}{\pi} y^2[1 + 4\bar{v}^*]j_3$	$c_6^* = -\frac{2}{5} y[1 + \frac{2}{\pi} \bar{v}^*](1 - \frac{15}{x^2} j_2)$
$c_7^* = -6y[1 + \frac{2}{\pi} \bar{v}^*]j_3/x$	$c_8^* = c_7^*$
$c_9^* = c_7^*$	$c_{10}^* = -6y[1 + \frac{2}{\pi} \bar{v}^*][j_2 - \frac{7}{x} j_3]$

Table 6.2 Small wavevector limits of the hydrodynamic coefficients.

$c_1^* \rightarrow -\frac{y}{5} [1 + \frac{20}{3\pi} \bar{v}^*]x^2$	$c_2^* \rightarrow -\frac{2}{15} [1 + \frac{1}{2} \bar{v}^*]x$
$c_3^* \rightarrow 0$	$c_4^* \rightarrow \frac{4}{175\pi} y^2[1 + 4\bar{v}^*]x^2$
$c_5^* \rightarrow 0$	$c_6^* \rightarrow -\frac{1}{35} y[1 + \frac{2}{\pi} \bar{v}^*]x^2$
$c_7^* \rightarrow -\frac{2}{35} y[1 + \frac{2}{\pi} \bar{v}^*]x^2$	$c_8^* \rightarrow c_7^*$
$c_9^* \rightarrow c_7^*$	$c_{10}^* \rightarrow 0$

coefficients is that they decay faster than x^{-2} for large x which contributes to the mode softening of generalized hydrodynamics which was alluded to in the introduction and which shall be explicitly presented in the next chapter.

CHAPTER 7

ANALYSIS OF THE SHORT TIME MODEL

In the previous chapter, we obtained the equations of a short time hydrodynamic model valid at large wavevector. In this chapter, we study the hydrodynamic modes of this model and compare them to the more familiar long wavelength hydrodynamic modes. The primary characteristic of equilibrium generalized hydrodynamics is a softening of the modes at large wavevector and we shall find that this is further enhanced at large shear rates to the point of creating an instability. We shall also find the appearance of new propagating modes at large shear rate.

Equilibrium Generalized Hydrodynamics

Before studying the effects of shear on the small wavelength hydrodynamics, we review equilibrium generalized hydrodynamics and compare it to ordinary hydrodynamics. If the shear rate is set equal to zero, the hydrodynamic matrix calculated in the previous chapter is found to be a function of $k\sigma$, where k is the magnitude of the wavevector and σ the hard sphere diameter, with no dependence on the direction of $\underline{k}$. It is also easy to see that the shear mode, momentum fluctuations in a direction perpendicular to the wavevector, decouple and is doubly degenerate as in the small- k limit (c.f., eq. (4.15)).

However, while the small k modes grow as k^2 , the generalized modes soften at large k and, in fact, the generalized heat mode is two orders of magnitude smaller at $k\sigma \sim 7$ than an extrapolation of its small k quadratic behavior would predict. For this reason, the relaxation time of hydrodynamic fluctuations on these length scales is much longer than one would expect and this explains how these microscopic modes can affect macroscopic properties. Figure 7.1 is a plot of the real parts of the equilibrium sound, heat and shear modes respectively for $no^3 = 0.88$. Figure 7.2 shows the equilibrium sound velocity as a function of $(k\sigma)$. These results agree well with the more detailed calculation of deSchepper and Cohen and support the extension of the present model to nonequilibrium situations.

The most striking feature of the generalized modes aside from their softening is that the sound mode becomes purely dissipative for $5.75 \leq k\sigma < 6.5$. In other words, for this range of wavevectors, sound does not propagate. Finally, we should note that these modes were calculated using the Carnahan-Starling expression for $\chi = g(\sigma)$ and the Percus-Yevick expression for the static structure factor, $S(\underline{k})$, with an approximate Verlet-Weiss correction.⁴⁶

Nonequilibrium Generalized Hydrodynamics

If we now vary the shear rate, we find several striking changes in the hydrodynamic modes. Before discussing these, however, we must note that the results to be presented here were obtained for the case $\underline{k} = \hat{k}y$. This choice of wavevector eliminates the gradient term in eq. (6.20) and reduces the problem of determining the modes to a simple

Fig. 7.1 Real parts of large wavevector heat, (H), sound, (S), and shear (SH) modes at equilibrium.

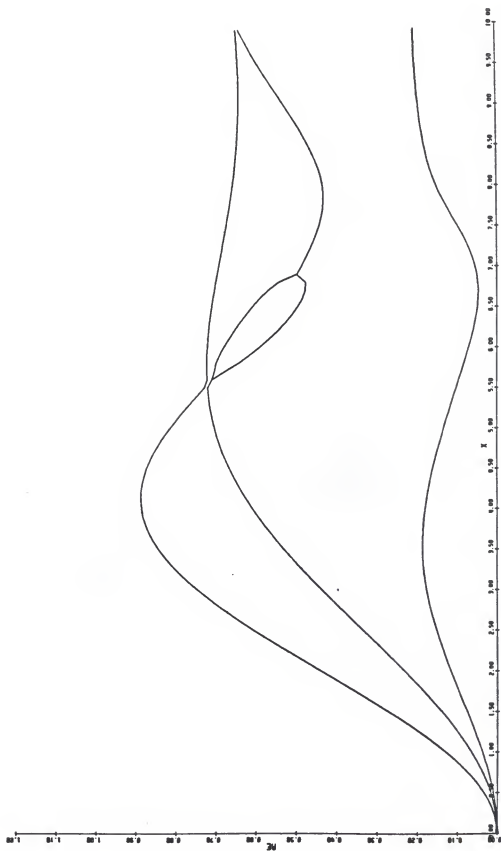
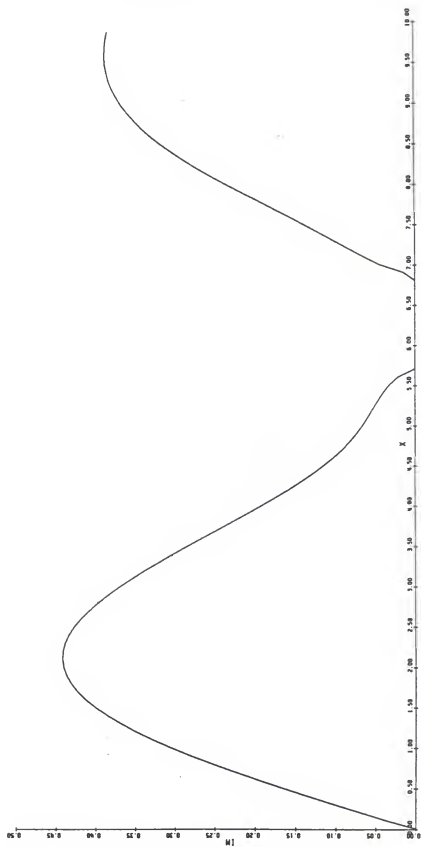


Fig. 7.2 Imaginary part of large wavevector sound mode.



eigenvalue problem. The case of wavevectors not along the y-axis can be studied using the methods presented in Chapter 4. However, the hydrodynamics at large wavevector is complicated even for the choice of wavevector used here and is representative of the effects to be found for other wavevectors so that the simplifying choice seems best. What is more, the results of Chapter 4 indicate that the slowest decaying modes will be those with $\underline{k}$ along the y-axis and so any instability in the system should occur for a lower shear rate than for any other direction of wavevector. Thus, we will henceforth take $\underline{k} = \hat{k}_y$ unless otherwise stated.

Figures 7.3 - 7.8 show the real parts of the sound, heat and shear modes for $a^* = a\tau_E = 0.1$ through 0.64 for $n^* \equiv n\sigma^3 = 0.88$. A peculiar feature of these modes is that above $a^* = 0.05$, there are two sets of propagating, or sound, modes for certain ranges of $k\sigma$. One set evolves from the equilibrium sound modes and is a shear rate dependent version of these modes. The other pair of propagating modes is the result of a shear induced mixing of the heat mode and one of the shear modes. As the figures show, the propagating modes appear and disappear and mix with one another as $k\sigma$ is varied.

For the density $n\sigma^3 = 0.88$, Fig. 7.8 shows that an instability exists for $k\sigma \approx 6.0$ and $a^* = 0.64$. In Fig. 7.9, we have plotted the critical shear rate (i.e., the minimum shear rate for which an instability exists) as a function of density. We believe this instability to be associated with the transition to the so-called string phase observed in computer simulations. Also shown in Fig. 7.9 are the two values of the critical shear rate as reported by Erpenbeck.¹²

Fig. 7.3 Real parts of large wavevector hydrodynamic modes, Re , vs. wavevector, $x = k\sigma$, for $a^* = 0.1$ and $n^* = 0.88$.

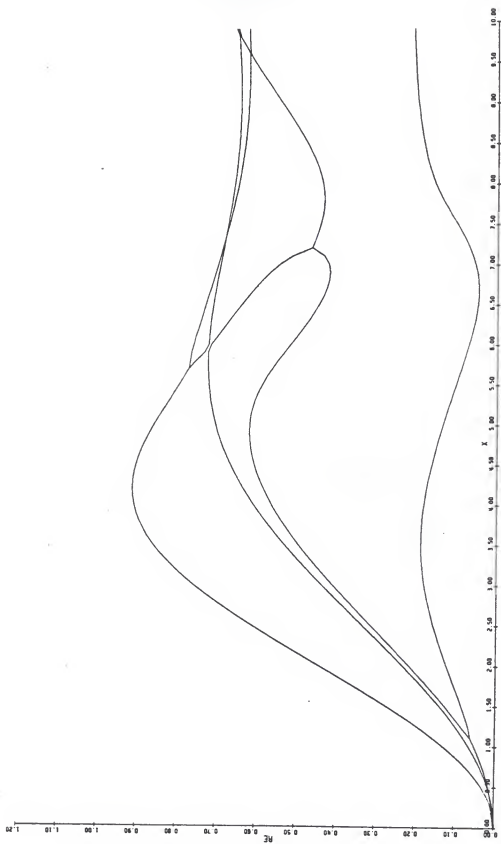


Fig. 7.4 Real parts of large wavevector hydrodynamic modes, Re , vs. wavevector, $x = k\sigma$, for $a^* = 0.2$ and $n^* = 0.88$.

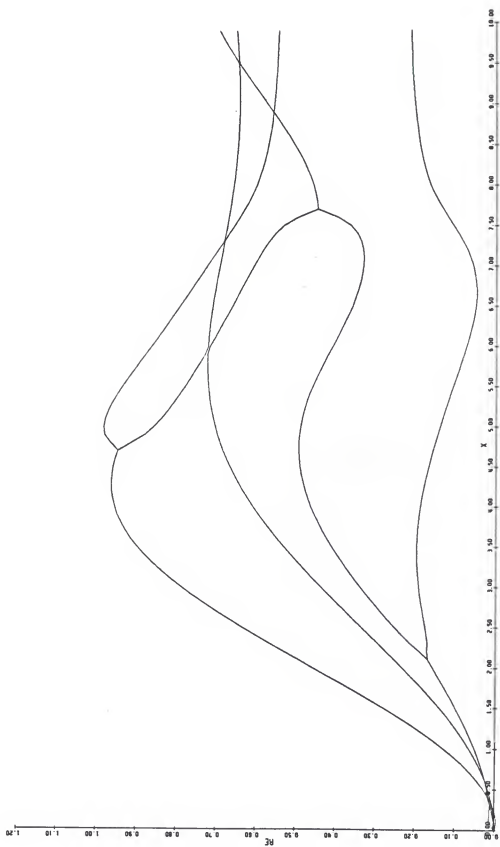


Fig. 7.5 Real parts of large wavevector hydrodynamic modes, Re , vs. wavevector, $x = k\sigma$, for $a^* = 0.3$ and $n^* = 0.88$.

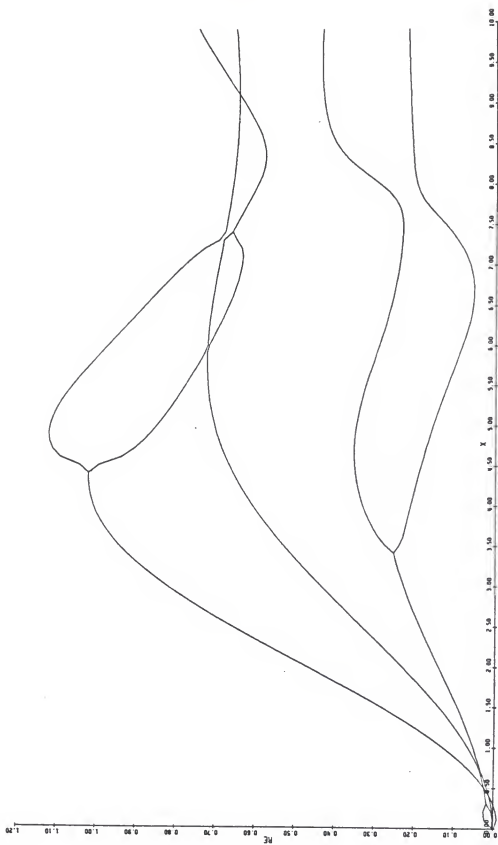


Fig. 7.6 Real parts of large wavevector hydrodynamic modes, Re , vs. wavevector, $x = k\sigma$, for $a^* = 0.4$ and $n^* = 0.88$.

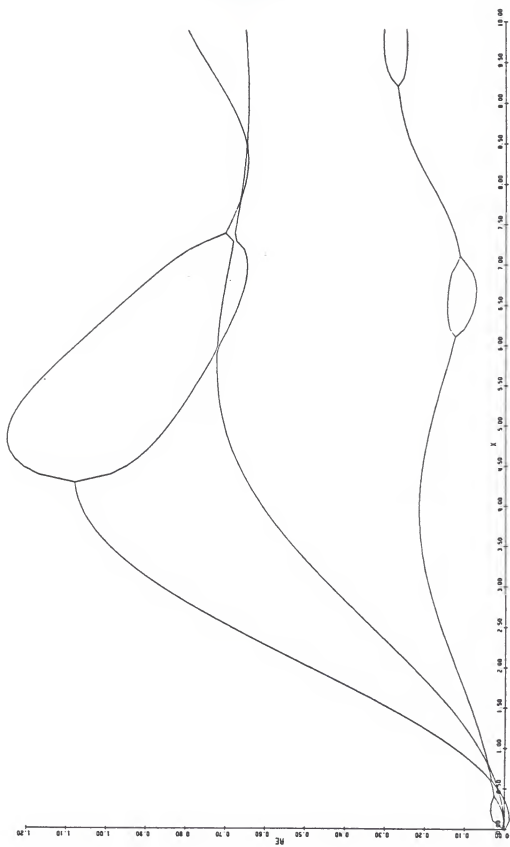


Fig. 7.7 Real parts of large wavevector hydrodynamic modes, Re , vs. wavevector, $x = ka$, for $a^* = 0.5$ and $\eta^* = 0.88$.

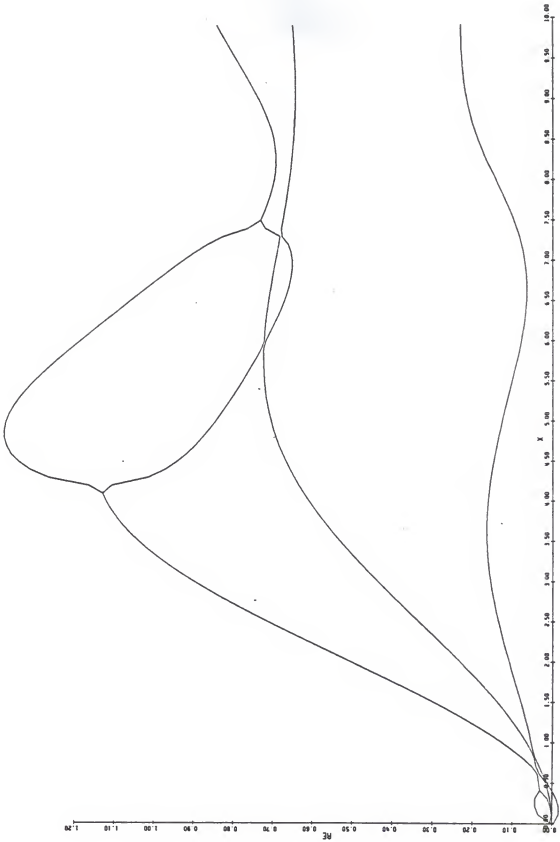


Fig. 7.8 Real parts of large wavevector hydrodynamic modes, Re , vs. wavevector, $x = k\sigma$, for $a^* = 0.63$ and $n^* = 0.88$.

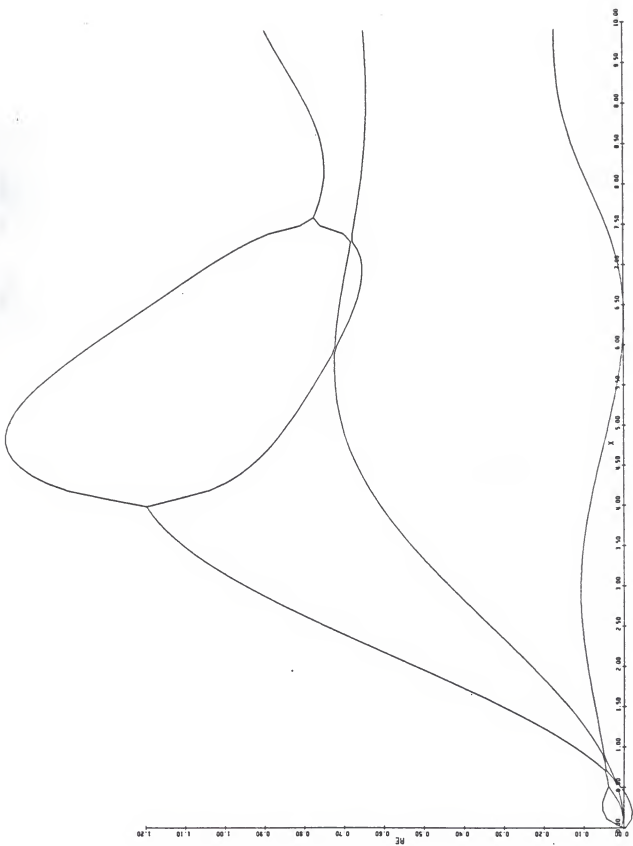
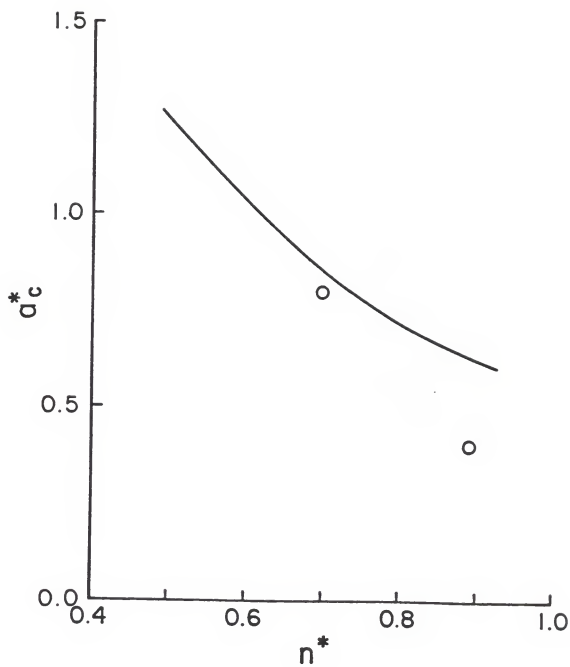


Fig. 7.9 Critical shear rate, a_c^* , as a function of reduced density, $n^* = n/n^*$. Also shown are Erpenbeck's values for the transition (o).



Numerically, Erpenbeck's values are about $a_c^* = 0.4$ and 0.8 for $n^* = 0.704$ and 0.88 , respectively. (There is some uncertainty in these numbers as the transition is not sharp.) Our values for these densities are $a_c^* = 0.63$ and 0.85 , respectively. Furthermore, S. Hess, in private conversation, has reported that the transition to the string phase is preceded by a transition from the amorphous fluid phase to a layered phase in which the hard spheres are partitioned into planes lying parallel to the x-z plane. This is consistent with the critical wavevector pointing in the y-direction since this indicates homogeneity in the x-z plane with variation in the y-direction. Finally, the eigenvector associated with the unstable mode is, in our calculation, almost a pure density mode while the partitioning into planes could be viewed as a phase transition in which the macroscopic density goes from being a constant, $\rho(\underline{r}) \sim \rho_0$, to being constant in the x-z plane and varying periodically in the y direction, $\rho(\underline{r}) \sim \rho_0' \sin^2 \pi y/d$ (where d is the interplane spacing).

The instability we observe is attributable primarily to a single element in the hydrodynamic matrix: the coupling of momentum fluctuations in the x-direction into the equation for momentum fluctuations in the y-direction (i.e., a coupling of transverse to longitudinal momentum fluctuations since $\underline{k} = \hat{k}\hat{y}$). This is easily ascertained in that when this coupling is set to zero, by hand, the minimum in the equilibrium heat mode remains unchanged as the shear rate is increased. From eq. (6.31), the coupling in question is seen

to be $a^*(c_6^* + c_9^*)$ which, from Table 6.2, is found to be proportional to $a^*(k\sigma)^2$ in the long wavelength limit. It thus is of third order in the gradients in this limit (n.b., $a \sim |\nabla u_0|$) and does not occur in the Navier-Stokes equations but, rather, in their generalization to include third order gradients which are known as the Burnett equations. This explains why the instability is not seen at small wavevectors (c.f., Chapter 4 in which the long wavelength equations are shown to be stable).

There is, however, a second instability at small (although not asymptotically small) wavevectors as seen in Figs. 7.3 - 7.9. We believe that this second instability is not seen in the simulations due to the fact that our calculations were performed for an infinite system while the simulations are necessarily done for finite systems. Applicability of our results requires that $\Delta k/k \ll 1$ where $\Delta k \sim 2\pi/L$, where L is the length of the box (for a finite system, the wavevector must be integral multiples of the "unit wavevector" Δk). For the simulations, $L^3 \sim N/n$ where N is the number of particles and n the density. Thus, applicability of our results requires that $(k\sigma) \gg 0.25$ for $n^*=0.88$ and $N=4000$ (the smallest Δk occurring in Erpenbeck's simulations). For wavevectors on the order of Δk , we expect that the boundary conditions, which we have not explicitly included in our calculation, become important. In fact, it is easy to understand physically both the nature of the instability and the reason it is not seen. It is found that this instability arises from the inertial (k -independent) momentum-momentum coupling in eq. (6.31). However, one can show that a zero-wavevector instability

arises from this coupling which is associated with center of mass motion. This zero-wavevector instability is unphysical, being prohibited by boundary conditions, and we conjecture the same is true of the small wavevector instability.

A similar calculation has been performed by Kirkpatrick⁴⁷ and Nieuwoldt (hereafter, KN). Two primary differences exist between our calculation and that of KN. The first is that KN neglect temperature fluctuations. We find in our model that the neglect of temperature fluctuations drastically alters the hydrodynamic modes and, in particular, gives rise to an unstable mode at small shear rate and both large and small wavevector. Thus, this approximation is unjustifiable in our model.

The second difference between our calculation and that of KN is that KN begin with the Enskog equation rather than the Liouville equation. They therefore approximate the nonequilibrium pair correlation function with its equilibrium form from the beginning. This means they have not built in information about the stationary state and as a consequence cannot use stationarity to eliminate the three-point function as we do. They are thus forced to use an approximation to the three-point function (specifically, they use the Kirkwood superposition approximation) which we do not need.

The result of these approximations is that KN sees an instability but at second order in the shear rate. There is an inconsistency, however, in that KN do not evaluate the effects of the thermostat which appears explicitly, at second order in the shear rate, in the

equations. Thus, the present calculation uses fewer assumptions than that of KN.

Finally, it would be very useful to obtain some idea of the completeness of the description of fluctuations presented here. The simplest check would be to study how well the hydrodynamic modes described here conform to those generated in the simulations. For instance, qualitatively, one might check whether there are indeed two sets of propagating modes at intermediate shear rates.

CHAPTER 8 CONCLUSIONS

The object of this thesis has been a description of fluctuations and transport in a sheared fluid. As was previously discussed, this system is particularly amenable to theoretical studies, both analytical and simulational, but is difficult to study experimentally. Experimental studies of more complicated systems are possible and many of the phenomena seen in the simulations of sheared simple fluids are also seen in laboratory experiments on these more complex systems. This agreement lends credence to the simulations which we thus use in place of experiment as a source of empirical data.

We began our theoretical study by restricting our attention to long wavelength fluctuations. These were described using fluctuating hydrodynamics generalized to the nonequilibrium state. The linear problem was solved under less restrictive conditions than had previously been used which allowed us to include states far from equilibrium in our analysis. Using our knowledge of the hydrodynamic modes, we investigated various statistical and physical properties of the fluid including the behavior of the time dependent correlation functions, the static correlation functions, the light scattering spectrum, and the distribution function. The most important consequences of the shear were due to the appearance of a gradient in

wavevector space in the linear equations (the linear mode coupling term). This term brings about a much faster decay of fluctuations and correlation functions than in equilibrium (an e^{-t^3} decay as opposed to e^{-t}). We also find long ranged correlations in the fluid.

Specifically, the equal time one dimensional correlation of densities decays as $x^{-5/3}$ indicating that the radial distribution function decays as $r^{-11/3}$ for large r .

We then proceeded to analyze the effect of the nonlinearities. These manifest themselves through a renormalization of the microscopic, bare, transport coefficients and susceptibilities. The renormalized shear viscosity was calculated using a "naive" method and found to be in agreement with previous calculations. This important concurrence indicates the equivalence of the presence model with those studied previously. A formal discussion of renormalization in this model was also presented. The formal scheme allows us to calculate renormalized properties other than the viscosity as well as providing a systematic means of studying higher order contributions.

In the final two sections, we studied the derivation and analysis of a model of small wavelength phenomena. It was found that the hydrodynamic modes were drastically modified by the shear and, in particular, that a large shear instability was found. The instability was proposed as the mechanism behind the transition to the string phase observed in simulations.

There is still much work to be done on this problem. In the fluctuating hydrodynamics problem, the nonlinear problem is still relatively unexplored. At a practical level, the complexity of the

correlation functions as determined from the linearized model makes the calculation of the renormalizations, even to lowest order, a difficult numerical problem. It would be of particular interest to calculate the renormalized shear viscosity from the formal theory without using local equilibrium correlation functions (c.f., the end of Chapter 5). More generally, the shear induces non-Gaussian statistics for the static fluctuations making this problem qualitatively different from most of those previously studied. The consequences of this difference remain unexplored.

In the short time model, several questions remain. One of the most important concerns the shear rate expansion. It is found that the shear rate is scaled to two different times: the Enskog time, t_E , and the Boltzmann time, $t_B = \chi t_E$, where for a dense fluid $\chi \sim 5$. The highest shear rate considered is at $t_B \sim 0.6$ (near the instability) or at $t_E \sim 0.1$. Thus, the expansion in at_E is quite reasonable while that in at_B is questionable. However, the at_B expansion arises solely from the expansion of the local equilibrium distribution function. If this expansion were not made, the elements of the hydrodynamic matrix would have to be calculated numerically. Such a calculation would provide a more quantitative description of the instability.

It would also be useful to understand the importance of momentum correlations. When we assumed a product form for the distribution function (c.f. eq. 6.22), we implicitly neglected momentum correlations. In equilibrium, this leads to a 50% error in the viscosity as calculated from the Enskog equation. We expect that an inclusion of these effects would produce quantitative changes in our

results. However, because the instability is due to the appearance of a new coupling, not present at long wavelengths, one might expect the qualitative result of the existence of an instability to be robust while the quantitative results as to the critical shear rate must be expected to be sensitive to changes in the model.

Finally, the methods used to study the long wavelength model could also be applied to the short time model. One might then calculate correlation functions, renormalized transport coefficients, etc. These calculations can be expected to produce results which may be compared to data compiled from simulations.

APPENDIX A
LINEARIZATION OF THE LANGEVIN EQUATION

The fluctuating hydrodynamics model was detailed in eqs. (3.23) - (3.29). We begin the linearization of this model by casting it in the form given in eq. (5.12),

$$\frac{\partial}{\partial t} y_m + V_m[y] + D_{mn}[y] F_n[y] = M_{mn}[y] \xi_n. \quad (\text{A.1})$$

This is accomplished by identifying,

$$V_\rho[y] = \nabla_\alpha j_\alpha$$

$$V_e[y] = \nabla_\alpha (e j_\alpha / \rho)$$

$$V_{j_\beta}[y] = \nabla_\alpha (p \delta_{\alpha\beta} + j_\alpha j_\beta / \rho), \quad (\text{A.2})$$

$$F_\rho[y] = - (\mu[y] - \frac{1}{2} j^2 / \rho) / T[y]$$

$$F_e[y] = 1/T[y]$$

$$F_{j_\alpha}[y] = - j_\alpha / (\rho T[y]) \quad (\text{A.3})$$

and all elements of D_{mn} zero except

$$D_{ee} = \nabla_{\alpha} T[y] \{T[y] \lambda[y] \delta_{\alpha\mu} + \eta_{\alpha\beta\mu\nu} [y] j_{\beta} j_{\nu} / \rho\} \nabla_{\mu}$$

$$D_{ej_{\nu}} = \nabla_{\alpha} T[y] \{ \eta_{\alpha\beta\mu\nu} [y] j_{\beta} / \rho \} \nabla_{\mu}$$

$$D_{j_{\nu}e} = D_{ej_{\nu}}$$

$$D_{j_{\beta}j_{\nu}} = \nabla_{\alpha} T[y] \{ \eta_{\alpha\beta\mu\nu} [y] \} \nabla_{\mu}. \quad (A.4)$$

In these equations, $T[y] = T_E[y]$ and $\mu[y] = \mu_E[y]$ where $T_E[y]$ is the equilibrium temperature functional, etc. The y -dependent transport coefficients are similarly defined in terms of their equilibrium analogs. Finally, in (A.4) we have abbreviated

$$\eta_{\alpha\beta\mu\nu} = \eta \Delta_{\alpha\beta\mu\nu} + \kappa \delta_{\alpha\beta} \delta_{\mu\nu} \quad (A.5)$$

with $\Delta_{\alpha\beta\mu\nu}$ as in eq. (3.41). The matrix M_{mn} is zero except

$$M_{e,1\alpha\beta} = - \nabla_{\alpha} \{ \eta[y] T[y] \}^{1/2} j_{\beta} / \rho$$

$$M_{e,2\alpha\beta} = - \nabla_{\alpha} \{ \kappa[y] T[y] \}^{1/2} j_{\beta} / \rho$$

$$M_{e,3\alpha} = - \nabla_{\alpha} \{ \lambda[y] k_B T^2[y] \}^{1/2}$$

$$\begin{aligned}
M_{j_{\alpha}, 1\beta\gamma} &= -\nabla_{\gamma}\{\eta[y] T[y]\}^{1/2} \delta_{\alpha\beta} \\
M_{j_{\alpha}, 2\beta\gamma} &= -\nabla_{\gamma}\{\kappa[y] T[y]\}^{1/2} \delta_{\alpha\beta}
\end{aligned}
\tag{A.6}$$

and

$$\begin{aligned}
\varepsilon_{1\alpha\beta} &= S_{1\alpha\beta} \\
\varepsilon_{2\alpha\beta} &= S_{2\alpha\beta} \\
\varepsilon_{3\alpha} &= S_{\alpha}.
\end{aligned}
\tag{A.7}$$

From eq. (3.29), we find $\Lambda_{mn} = 0$ except

$$\begin{aligned}
\Lambda_{1\alpha\beta, 1\mu\nu} &= \Delta_{\alpha\beta\mu\nu} \\
\Lambda_{2\alpha\beta, 2\mu\nu} &= \delta_{\alpha\beta} \delta_{\mu\nu} \\
\Lambda_{3\alpha, 3\beta} &= \delta_{\alpha\beta}.
\end{aligned}
\tag{A.8}$$

With these definitions, it is easy to verify that the fluctuation-dissipation relation, eq. (5.13), is verified.

Although this model could be studied as it stands, we wish to consider a restricted model in which only quadratic nonlinearities arising from the convective terms, i.e., those in (A.2), are kept. Thus, the restricted model is obtained by making the substitutions;

$$D_{mn}[y] + D_{mn}[y_0]$$

$$F_m[y] + F_m[y_0] + \frac{\delta F_m}{\delta y} \Big|_{y_0} \delta y$$

$$M_{mn}[y] + M_{mn}[y_0] \quad (A.9)$$

where $\delta y = y - y_0$ and the convective terms to second order (except the pressure which, as in equilibrium calculations, is only expanded to first order). With these substitutions, it is found that the fluctuation-dissipation theorem is preserved up to and including $\sigma(k^2)$. The resulting equations are

$$\frac{\partial}{\partial t} z_a - a_{ij} k_i \frac{\partial}{\partial k_j} z_a + H_{ab}(\underline{k}; a) z_b + V_{abc}(\underline{k}, \underline{q}_1, \underline{q}_2) (z_b(\underline{q}_1) z_c(\underline{q}_2) - \langle z_b(\underline{q}_1) z_c(\underline{q}_2) \rangle)$$

$$= R_a(\underline{k}, t) \quad (A.10)$$

where

$$H_{ab}(\underline{k}; a) = k H_{ab}^{(0)}(\underline{k}) + k^2 H_{ab}^{(1)}(\underline{k}) + a H_{ab}^{(2)}(\underline{k})$$

$$L_{ab}^{(0)}(\hat{k}) = \begin{pmatrix} 0 & 0 & i\rho_0 c_1 & 0 & 0 \\ 0 & 0 & i h_0 c_2 & 0 & 0 \\ i\rho_0 c_1 & i h_0 c_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$L_{ab}^{(1)} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ c_3 \lambda_0 & c_4 \lambda_0 & 0 & 0 & 0 \\ 0 & 0 & v_0' & 0 & 0 \\ 0 & 0 & 0 & v_0 & 0 \\ 0 & 0 & 0 & 0 & v_0 \end{pmatrix}$$

$$L_{ab}^{(2)}(\hat{k}) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \Gamma_{11} & \Gamma_{12} & \Gamma_{13} \\ 0 & 0 & \Gamma_{21} & \Gamma_{22} & \Gamma_{23} \\ 0 & 0 & \Gamma_{31} & \Gamma_{32} & \Gamma_{33} \end{pmatrix} \quad (A.11)$$

where λ_0 is the thermal conductivity, $v_0 = \eta_B / \rho_0$ is the kinematic viscosity, $v_0' = \frac{4}{3} v_0 + \rho_0^{-1} \kappa_B$ and

$$a\Gamma_{ij} = \hat{e}_i^{(1)}(\underline{k}) a_{lm} \hat{e}_m^{(j)}(\underline{k}) - a_{lm} k_l \hat{e}_n^{(i)}(\underline{k}) \frac{\partial}{\partial k_m} \hat{e}_n^{(j)}(\underline{k}). \quad (A.12)$$

The vertices are

$$V_{abc}(\underline{k}, q_1, q_2) = \delta(\underline{k} - q_1 - q_2) (A_{abc}(\underline{k}, q_1) + A_{acb}(\underline{k}, q_2))$$

$$\begin{aligned}
& - \frac{1}{2} \delta_{ab} \hat{e}_{\alpha}^{(c-2)}(\underline{k}-\underline{q}) k_{\alpha} & a=1,2 & b,c=3-5 \\
A_{abc}(\underline{k},\underline{q}) = & - \frac{1}{2} \hat{e}_{\alpha}^{(a)}(\underline{k}) \hat{e}_{\alpha}^{(b)}(\underline{q}) k_{\beta} \hat{e}_{\beta}^{(c)}(\underline{k}-\underline{q}) & a=3-5 & b,c=3-5 \\
& 0 & & b,c < 3.
\end{aligned}
\tag{A.13}$$

and where we have introduced a change of variables $y \rightarrow w \rightarrow z$. The change $y \rightarrow w$ is defined by replacing the momentum density, j_{α} , with the local velocity fluid, u_{α} , and the total energy density, e , with the internal energy density, ϵ , where

$$\begin{aligned}
\hat{j}_{\alpha} &= \hat{\rho} \hat{u}_{\alpha} \\
\hat{e} &= \frac{1}{2} \hat{\rho} \hat{u}^2 + \hat{\epsilon}.
\end{aligned}
\tag{A.14}$$

We note that

$$\begin{aligned}
\langle \hat{j}_{\alpha} \rangle &= j_{0\alpha} = \rho_0 \underline{a} \cdot \underline{r} \\
\langle \hat{e} \rangle &= e_0 = \frac{1}{2} \rho_0^{-1} j_0^2 + \epsilon_0
\end{aligned}
\tag{A.15}$$

so,

$$\langle \hat{u}_\alpha \rangle = u_{0\alpha} = \frac{a}{\rho} \cdot \underline{r} + \langle \hat{j}/\rho - j_0/\rho_0 \rangle$$

$$\langle \hat{\epsilon} \rangle = \epsilon'_0 = \epsilon_0 + \langle \hat{e} - e_0 \rangle. \quad (\text{A.16})$$

The second change of variables, $w \rightarrow z$, is defined by

$$z_1 = c_1(\hat{\rho} - \rho_0)$$

$$z_2 = c_2(\hat{\epsilon} - \epsilon_0)$$

$$z_{3+i} = \hat{e}_{\alpha}^{(i)}(\underline{k})(u_\alpha - u_{0\alpha}) \quad (\text{A.17})$$

where $\{\hat{e}^{(i)}(\underline{k})\}$ is a set of three mutually orthogonal unit vectors

with $\hat{e}^{(1)}(\underline{k}) = \hat{k} = \underline{k}/k$ and

$$c_0^2 = (\rho_0 c_1)^2 + (h_0 c_2)^2 = \frac{\partial p_0}{\partial \rho_0} \Big|_{s_0}$$

$$c_1^2 = \rho_0^{-2} \frac{\partial p_0}{\partial \rho_0} \Big|_{\epsilon_0} = \frac{c_0^2}{\rho_0^2} \left[1 - \frac{\alpha_T}{\rho_0 c_p} h_0 \right]$$

$$c_2^2 = (\rho_0 h_0)^{-1} \frac{\partial p_0}{\partial \epsilon_0} \Big|_{\rho_0} = \frac{c_0^2 \alpha_T}{\rho_0 h_0 c_p}. \quad (\text{A.18})$$

In these equations, $\alpha_T = \rho_0^{-1} (\partial \rho_0 / \partial T_0) / p$ is the thermal expansion

coefficient, c_p is the constant pressure specific heat, c_0 is the sound velocity and h_0 is the enthalpy density. For later reference, we also define

$$c_3 = \frac{c_2}{c_1} \frac{\partial T_0}{\partial \rho_0} \Big|_{\epsilon_0} = \frac{c_2}{c_1} \left[\frac{\gamma-1}{\rho_0 \alpha_T} - \frac{h_0}{\rho_0 c_v} \right]$$

$$c_4 = \frac{\partial T_0}{\partial \epsilon_0} \Big|_{\rho_0} = \frac{1}{\rho_0 c_v} \quad (\text{A.19})$$

where c_v is the constant volume specific heat and $\gamma = c_p/c_v$.

Finally, the fluctuating forces appearing in (A.10) have correlations,

$$\langle R_a(\underline{k}, t) \rangle = 0$$

$$\langle R_2(\underline{k}, t) R_2(\underline{k}', t') \rangle = (2\pi)^3 (c_1^2 - 2 \kappa_B T_0^2 \lambda_0) k^2 \delta(\underline{k} + \underline{k}') \delta(t - t')$$

$$\langle R_a(\underline{k}, t) R_b(\underline{k}', t') \rangle = (2\pi)^3 [2 \kappa_B T_0 (2 \eta_B \delta_{a3} \delta_{b3} + (\kappa_B - \frac{2}{3} \eta_B) \delta_{ab})$$

$$\times k^2 \delta(\underline{k} + \underline{k}') \delta(t - t')] \quad (\text{A.20})$$

where $a, b = 3-5$ and all other cumulants are zero (i.e., $\langle\langle o(k^2) \rangle\rangle$).

APPENDIX B GENERALIZED EIGENVALUE PROBLEM

The generalized eigenvalue problem is

$$-a_{ij} k_i \frac{\partial}{\partial k_j} \xi_a^{(\alpha)}(\underline{k}; a) + H_{ab}(\underline{k}; a) \xi_b^{(\alpha)}(\underline{k}; a) = \lambda^{(\alpha)}(\underline{k}; a) \xi_a^{(\alpha)}(\underline{k}; a). \quad (B.1)$$

We solve this equation perturbatively recalling that

$$ck \gg vk^2 \sim a. \quad (B.2)$$

Thus, we expect the eigenvectors and eigenvalues as

$$\begin{aligned} \underline{\xi}^{(\alpha)} &= \underline{\xi}_0^{(\alpha)} + k \underline{\xi}_1^{(\alpha)} + \dots \\ \lambda^{(\alpha)} &= k \lambda_1^{(\alpha)} + k^2 \lambda_2^{(\alpha)} + \dots \end{aligned} \quad (B.3)$$

The lowest order equation is

$$H_{iab} \xi_{0b}^{(\alpha)} = \lambda_1^{(\alpha)} \xi_{0a}^{(\alpha)}. \quad (B.4)$$

The eigenvalues and eigenvectors of H_1 are found to be

$$\lambda_0^{(1)} = -ic_0 = -\lambda_0^{(2)}$$

$$\lambda_0^{(3)} = 0 = \lambda_0^{(4)} = \lambda_0^{(5)} \quad (\text{B.5})$$

with

$$\psi^{(1)} = \frac{1}{\sqrt{2} c_0} (\rho_0 c_1, h_0 c_2, c_0, 0, 0)$$

$$\psi^{(2)} = \frac{1}{\sqrt{2} c_0} (\rho_0 c_1, h_0 c_2, -c_0, 0, 0)$$

$$\psi^{(3)} = \frac{1}{c_0} (h_0 c_2, -\rho_0 c_1, 0, 0, 0)$$

$$\psi^{(4)} = (0, 0, 0, 1, 0)$$

$$\psi^{(5)} = (0, 0, 0, 0, 1). \quad (\text{B.6})$$

These vectors are, in fact, orthogonal. Because of the degeneracy, we find that

$$\xi_0^{(1)} = \psi^{(1)}$$

$$\xi_0^{(2)} = \psi^{(2)}$$

$$\xi_0^{(\alpha)} = A_{\alpha\beta} \psi^{(\beta)}, \quad \alpha, \beta = 3-5 \quad (\text{B.7})$$

where $A_{\alpha\beta}$ is to be determined at next order.

The second order equations are

$$H_{1ab} \xi_{1b}^{(\alpha)} = \lambda_2^{(\alpha)} \xi_{0a}^{(\alpha)} + \lambda_1^{(\alpha)} \xi_{1a}^{(\alpha)} + k^{-2} a_{ij} k_i \frac{\partial}{\partial k_j} \xi_{0a}^{(\alpha)} + (H_{2ab} + k^{-2} a H_{3ab}) \xi_{ab}^{(\alpha)}. \quad (B.8)$$

Multiplying through by $\psi_a^{(\beta)}$ and summing on a , we find immediately that

$$\lambda_2^{(1)} = \lambda_2^{(2)} = \frac{1}{2} (\Gamma_0 + ak^{-2} \Gamma_{11}) \quad (B.9)$$

where

$$\Gamma_0 = \frac{h_0 \lambda_0 c_2}{2} (\rho_0 c_1 c_3 + h_0 c_2 c_4) + v'_0 = \frac{c_p}{c_v} D_T + v'_0 \quad (B.10)$$

is the sound damping constant and D_T is the thermal diffusivity. For $\alpha, \beta = 3-5$, one obtains

$$[\psi_a^{(\beta)} (H_{2ab} + ak^{-2} H_{3ab}) \psi_b^{(\sigma)} - a_{ij} k^{-2} \frac{\partial}{\partial k_j} \delta_{\sigma\beta} + \lambda_1^{(\alpha)} \delta_{\sigma\beta}] A_{\alpha\sigma} = 0. \quad (B.11)$$

Now,

$$\psi_a^{(3)} (H_{2ab} + ak^{-2} H_{3ab}) \psi_b^{(\sigma)} = \delta_{3\sigma} D_T. \quad (B.12)$$

So one solution of eq. (B.12) for $\alpha=3$ is

$$\lambda_1^{(3)} = D_T$$

$$A_{3\sigma} = \delta_{3\sigma}. \quad (\text{B.13})$$

Equation (B.11) then becomes

$$\begin{aligned} [\lambda_1^{(\alpha)} k^2 - v_0 k^2 - a\Gamma_{22} + ak_x \frac{\partial}{\partial k_y}] A_{\alpha 4} &= 0 \\ [\lambda_1^{(\alpha)} k^2 - v_0 k^2 + ak_x \frac{\partial}{\partial k_y}] A_{\alpha 5} - a\Gamma_{32} A_{\alpha 4} &= 0 \end{aligned} \quad (\text{B.14})$$

which is solved by

$$\begin{aligned} A_{44} &= 1 & A_{45} &= \hat{A}(k) \\ A_{54} &= 0 & A_{55} &= 1 \\ \hat{A}(k) &= \frac{k_z}{k_x k_{\perp}} \tan^{-1}(k_y/k_{\perp}) \\ k_{\perp}^2 &= k_x^2 + k_y^2. \end{aligned} \quad (\text{B.15})$$

This is not the general solution to (B.14) and is clearly not defined at $k_x = 0$. However, it is possible to show that the Green's function

is independent of the particular solution to (B.14) chosen and is well defined even at $k_x = 0$.

Thus, to order k^2 ,

$$\lambda_1 = -ick + \frac{1}{2} \Gamma_0 k^2 + \frac{1}{2} a k_x k_y / k^2$$

$$\lambda_2 = \lambda_1^*$$

$$\lambda_3 = D_T k^2$$

$$\lambda_4 = v_0 k^2 - a k_x k_y / k^2$$

$$\lambda_5 = v_0 k^2 \quad (\text{B.16})$$

and, to lowest order,

$$\xi^{(\alpha)} = \psi^{(\alpha)} \quad \alpha = 1-3$$

$$\xi^{(4)} = (0, 0, 0, 1, \hat{A}(k))$$

$$\xi^{(5)} = (0, 0, 0, 0, 1) \quad (\text{B.17})$$

and the set of vectors bi-orthonormal to $\{\xi^{(\alpha)}\}$, $\{\eta^a\}$ where $\eta_a^{(\alpha)} \xi_a^{(\beta)} = \delta_{\alpha\beta}$, is to lowest order,

$$\eta^{(\alpha)} = \psi^{(\alpha)} \quad \alpha = 1-3$$

$$\eta^{(4)} = (0, 0, 0, 1, 0)$$

$$\eta^{(5)} = (0, 0, 0, -A, 1). \quad (\text{B.18})$$

APPENDIX C DYNAMIC STRUCTURE FACTOR

The dynamic structure factor, $S(\underline{k}, \omega)$, was defined in eq. (4.47) to be

$$\begin{aligned} S(\underline{k}, \omega) &= \int_{-\infty}^{\infty} dt \int \frac{d\underline{k}_1 d\underline{k}_2}{(2\pi)^6} \tilde{o}(\underline{k}-\underline{k}_1) \tilde{o}(\underline{k}+\underline{k}_2) C_{\rho\rho}(\underline{k}_1, t; \underline{k}_2, 0) e^{i\omega t} \\ &= 2\text{Re} \int_0^{\infty} dt \int \frac{d\underline{k}_1 d\underline{k}_2}{(2\pi)^6} \tilde{o}(\underline{k}-\underline{k}_1) \tilde{o}(\underline{k}+\underline{k}_2) C_{\rho\rho}(\underline{k}_1, t; \underline{k}_2, 0) e^{i\omega t}. \end{aligned} \quad (\text{C.1})$$

Using eqs. (4.36) and (4.39), this may be written in the form

$$\begin{aligned} S(\underline{k}, \omega) &= 2\text{Re} \int \frac{d\underline{k}_1}{(2\pi)^3} \tilde{o}(\underline{k}-\underline{k}_1) \xi_1^{(a)}(\underline{k}_1) \sigma^{(a)}(\underline{k}, \underline{k}_1; \omega) \\ &= \sum_{a=1}^3 S^{(a)}(\underline{k}, \omega) \end{aligned} \quad (\text{C.2})$$

with $\sigma^{(a)}$ the solution to

$$\begin{aligned} [-i\omega + \lambda^{(a)}(\underline{k}_1; a) - a_{ij} k_{1i} \frac{\partial}{\partial k_{1j}}] \sigma^{(a)}(\underline{k}, \underline{k}_1; \omega) = \\ c_1^{-2} \tilde{o}(\underline{k}-\underline{k}_1) \eta_a^{(a)}(\underline{k}_1) c_{a1}(\underline{k}_1; a). \end{aligned} \quad (\text{C.3})$$

Multiplying (C.3) by $\xi_1^{(a)}(\underline{k})\bar{\sigma}(\underline{k}-\underline{k}_1)$, integrating over $\underline{k}_1$ and integrating by parts the gradient term yields

$$\int \frac{d\underline{k}_1}{(2\pi)^3} \bar{\sigma}^2(\underline{k}-\underline{k}_1) \left\{ [-i\omega + \lambda^{(a)}(\underline{k}_1; a) - \frac{1}{2} a_{ij} k_{1i} \frac{\partial}{\partial k_j}] \bar{\sigma}^{(a)}(\underline{k}_1; \omega) - \xi_1^{(a)} \eta_\alpha^{(a)} c_1^{-2} c_{\alpha 1}(\underline{k}_1; a) \right\} = 0 \quad (C.4)$$

where we have defined $\xi_1^{(a)} \sigma^{(a)}(\underline{k}, \underline{k}_1; \omega) = \bar{\sigma}(\underline{k}-\underline{k}_1) \bar{\sigma}^{(a)}(\underline{k}_1; \omega)$ and we have used the fact that the shear modes do not contribute so the eigenvectors appearing here are $\underline{k}$ -independent. Equation (C.4) can be written as

$$\int \frac{d^3 k}{(2\pi)^3} \bar{\sigma}^2(\underline{k}_1) \left\{ [-i\omega + \lambda^{(a)}(\underline{k}+\underline{k}_1; a) - \frac{1}{2} a_{ij} (\underline{k}+\underline{k}_1)_i \frac{\partial}{\partial k_j}] \bar{\sigma}^{(a)}(\underline{k}+\underline{k}_1; \omega) - \xi_1^{(a)} \eta_\alpha^{(a)} c_1^{-2} c_{\alpha 1}(\underline{k}+\underline{k}_1; a) \right\} = 0. \quad (C.5)$$

In terms of $\bar{\sigma}^{(a)}(\underline{k}, \omega)$, $S^{(a)}(\underline{k}, \omega)$ is

$$S^{(a)}(\underline{k}, \omega) = \int \frac{d\underline{k}_1}{(2\pi)^3} \bar{\sigma}^2(\underline{k}_1) \bar{\sigma}^{(a)}(\underline{k}+\underline{k}_1; \omega). \quad (C.6)$$

Now, the wavelength of the light is usually much less than the length of the illuminated volume so, in (C.5) and (C.6),

$$k \gg k_1 \quad (C.7)$$

yielding the approximate equations,

$$S^{(a)}(\underline{k}, \omega) = \bar{\sigma}^{(a)}(\underline{k}; \omega)$$

$$[-i\omega + \lambda^{(a)}(\underline{k}, \omega) - \frac{1}{2} a_{1j} k_1 \frac{\partial}{\partial k_j}] \bar{\sigma}^{(a)}(\underline{k}, \omega) = \xi_1^{(a)} \eta_\alpha^{(a)} c_1^{-2} C_{\alpha 1}(\underline{k}; a)$$

(C.8)

The right side of (C.8) is the same for $a = 1$ and 2 so

$$S^{(1)}(\underline{k}, \omega) = S^{(2)}(\underline{k}, -\omega) = S^B(\underline{k}, \omega).$$

APPENDIX D ELIMINATION OF THE THREE POINT FUNCTION

Upon making the factorization approximation in eq. (6.22), it is clear that only the $\beta=1$ term contributes. Returning to eq. (6.21) and using the adjoint of the Liouville operator we find that

$$\langle (\hat{\mathcal{L}}_+ y_\alpha(\underline{k})) \delta y_\beta(\underline{k}) \rangle_{ss} = \langle y_\alpha(\underline{k}) (\hat{\mathcal{L}}_- \delta y_\beta(\underline{k})) \rangle_{ss} \quad (D.1)$$

and for $\beta=1$, we have

$$\hat{\mathcal{L}}_- \delta y_1(\underline{k}) = (\hat{\mathcal{L}}_-)_0 \delta y_1(\underline{k}) + (\hat{\mathcal{L}}_-)_{int} \delta y_1(\underline{k}) + (\hat{\mathcal{L}}_-)_{ext} \delta y_1(\underline{k}) \quad (D.2)$$

where

$$\begin{aligned} (\hat{\mathcal{L}}_-)_0 \delta y_1(\underline{k}) &= -ik_j \delta y_{2+j}(\underline{k}) \\ (\hat{\mathcal{L}}_-)_{int} \delta y_1(\underline{k}) &= 0 \\ (\hat{\mathcal{L}}_-)_{ext} \delta y_1(\underline{k}) &= 0. \end{aligned} \quad (D.3)$$

So,

$$\langle (\hat{\mathbf{f}}_+ \cdot \mathbf{y}_\alpha(\underline{k})) \delta y_1(\underline{k}) \rangle = -1 \sum_{j=1}^3 k_j g_{\alpha, 2+j}(\underline{k}) \quad (\text{D.4})$$

and, from eq. (6.12),

$$L_{\alpha 1}(\underline{k}, \underline{k}'; a) = L_{\alpha 1}(\underline{k}; a) \delta(\underline{k} - \underline{k}') \quad (\text{D.5})$$

where

$$L_{\alpha 1}(\underline{k}; a) = -1 \sum_{j=1}^3 k_j g_{\alpha, 2+j}(\underline{k}) / g_{11}(\underline{k}). \quad (\text{D.6})$$

So, finally, using the explicit form of $g_{\alpha\beta}(\underline{k})$, eq. (6.27),

$$L_{11}(\underline{k}; a) = L_{21}(\underline{k}; a) = 0$$

$$L_{\alpha 1}(\underline{k}; a) = -\frac{ik}{nS(\underline{k})} \{ \rho_0 k_B T_0 \hat{k}_{\alpha-2} - mn_0 (\delta_{\alpha,3} \hat{k}_y + \delta_{\alpha,4} \hat{k}_x) \}. \quad (\text{D.7})$$

We also note here that the source in eq. (6.30) is easy to evaluate to lowest order in the shear if we note that

$$\begin{aligned} \hat{\mathbf{f}}_{\text{ext}} \cdot \hat{\mathbf{y}}_\alpha(\underline{k}) &= 0 & \alpha=1 \\ &= 2\lambda(\Gamma) [y_2(\underline{k}) + (\frac{3}{2} k_B T) y_1(\underline{k})] & \alpha=2 \\ &= \lambda(\Gamma) y_\alpha(\underline{k}) & \alpha=3 \end{aligned} \quad (\text{D.8})$$

and because $\lambda(r) \ll a$, we can set $a=0$ in all other quantities, including the distribution function, when calculating the lowest order contribution in the shear rate. Thus,

$$S_{1\beta} = 0$$

$$S_{2\beta} = 2\langle \lambda(r) y_2(\underline{k}) \delta y_\beta(-\underline{k}) \rangle_{eq} + \frac{3}{2} (k_B T_0) \langle \lambda(r) y_1(\underline{k}) \delta y_\beta(\underline{k}) \rangle_{eq} + o(a^2)$$

$$S_{\alpha\beta} = \langle \lambda(r) \delta y_\alpha(\underline{k}) \delta y_\beta(-\underline{k}) \rangle_{eq} + o(a^2), \quad \alpha=3-5 \quad (D.9)$$

where, as indicated, the averages are now done in equilibrium and $y_\alpha(\underline{k})$ is evaluated at $a=0$ for all α . Now, to lowest order in the shear,

$$\lambda(r) = -a \sum_j p_{jx} p_{jy} / \sum_l p_l^2, \quad (D.10)$$

so the angular averages require that

$$S_{2\beta} = 0$$

$$S_{\alpha\beta} = -a \langle \sum_j p_{jx}^2 p_{jy}^2 / \sum_j p_j^2 \rangle_{eq} (\delta_{\alpha 3} \delta_{\beta 4} + \delta_{\alpha 4} \delta_{\beta 3}) \quad (D.11)$$

to first order in the shear. This is easily evaluated to give

$$S_{\alpha\beta} = - (4 m^2 N k_B T) a (\delta_{\alpha 3} \delta_{\beta 4} + \delta_{\alpha 4} \delta_{\beta 3}) \quad \alpha, \beta=3-5 \quad (D.12)$$

and, the contribution to the hydrodynamic matrix, $H_{\alpha\beta}^{(s)}$, is

$$\begin{aligned}
 H_{\alpha\beta}^{(s)} &= S_{\alpha\sigma} (g^{-1})_{\sigma\beta} \\
 &= - (4 m^2 N k_B T) a (\delta_{\alpha 3} \delta_{\sigma 4} + \delta_{\alpha 4} \delta_{\sigma 3}) (g^{-1})_{\sigma\beta} + o(a^2). \quad (D.13)
 \end{aligned}$$

But, to lowest order in the shear, $(g^{-1})_{\sigma\beta} = \delta_{\sigma\beta}$ for $\sigma = 3$ or 4 .

Thus,

$$H_{\alpha\beta}^{(s)} = o(a^2). \quad (D.14)$$

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BIOGRAPHICAL SKETCH

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



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A handwritten signature in dark ink, appearing to read "J. Hammack", is written over a horizontal line.

J. Hammack
Professor of Engineering Sciences

This dissertation was submitted to the Graduate Faculty of the Department of Physics in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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